Development of (TAML) iron complexes for photocatalytic, oxidative water treatment

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NANYANG
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**DEVELOPMENT OF (TAML)IRON COMPLEXES
FOR PHOTOCATALYTIC, OXIDATIVE WATER
TREATMENT**

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FOR PHOTOCATALYTIC, OXIDATIVE WATER
TREATMENT**

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Energy Research Institute @ NTU (ERI@N)**

**A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy**

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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Student Name

Abstract

The current energy demand is met mainly by the combustion fossil fuels. This unsustainable energy source brings about negative environmental effects. Using solar energy for water treatment is an appealing solution. To achieve this undertaking, we hypothesized that (TAML)Fe caomplexes, which have been reported to be excellent catalysts for the degradation of persistent pollutants, can be activated photochemically, when coupled with suitable photosensitizers in the right conditions.

The project began with the syntheses of the previously reported (TAML)Fe (**1**), a new (TAML-COOMe)Fe (**2**), and a new (TAML-COOH)Fe (**3**). We uncovered a new synthetic route that utilizes nitroaniline precursors instead of *o*-phenylenediamines, enabling access to a wider range of (TAML) ligand systems.

Subsequently, we characterized the electrochemical properties of complexes **1** and **2** using cyclic voltammetry. We have shown that Ru(bpy)₃²⁺ should be a suitable photosensitizer to oxidize **1** and **2** photochemically. Hence, we performed transient absorption spectroscopic (TAS) experiments on **1** in a Ru(bpy)₃²⁺/Co(CH₃)₅Cl₃ photosensitizer system. The TAS results have verified that the Ru(bpy)₃²⁺/Co(NH₃)₅Cl₃ photosensitizer system is able to oxidize **1** by at least one electron, producing a relatively long-lived oxidized **1** intermediate. The CV results also suggested the possibility of accessing a rarely reported three-electron oxidized **2** (formally Fe^{VI} complex). Thus we oxidized **2** electrochemically and chemically at low temperatures. The preliminary results indicate that the three-electron oxidized **2** (**2**³⁺) may have been generated, and efforts to characterize this intermediate spectroscopically and by X-ray crystallography are still ongoing.

However, the oxidation of **1** by the $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system gave rise to an anion-dependent valence tautomerization of the oxidized **1** intermediate. Through mechanistic studies, kinetics measurements, mass spectrometry, and Mössbauer spectroscopy, we showed that ligand-based oxidation occurs to give **1-TAML•⁺** in equilibrium with Fe^{IV} , instead of the conventional electrophilic halide reactivity. The extent of valence tautomerization depends on the exogenous anions present. A strongly-coordinating CN^- will become an axial ligand to stabilize Fe^{IV} , and we have isolated and structurally characterized an unprecedented dicyano (TAML) Fe^{IV} complex. On the other hand, labile halides favor the Fe^{III} **1-TAML•⁺** tautomer, which is susceptible to nucleophilic substitution on the ligand.

Finally, we anchored **3** on $g\text{-C}_3\text{N}_4$ as a photosensitizer, and characterized the $g\text{-C}_3\text{N}_4\text{-3}$ composite using DRS, IR spectroscopic, and XAS measurements. Photocatalytic degradation experiments suggested that **3**, after being oxidized by the hole(s) from the VB of $g\text{-C}_3\text{N}_4$, might have recombined faster with the electrons in the CB. To further minimize the effect of charge recombination, we adopted a photoelectrochemical approach and used an electric field instead of a chemical electron acceptor. We also improved the poor interfacial charge transfer from $g\text{-C}_3\text{N}_4$ to the FTO electrode by annealing the $g\text{-C}_3\text{N}_4$ onto FTO glass before doping it with **3**. Preliminary evaluations of the electrodes using CV and photoelectrical experiments showed that the doping of the annealed FTO- $g\text{-C}_3\text{N}_4$ electrode with **3** lowered the onset potential and increased the amount of photocurrent. These promising results have propelled us to explore the photoelectrocatalytic degradation of pollutants.

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Figure Captions

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Figure 4.10 Scheme summarizing the findings from TAS experiments.

Figure 4.11 (a) UV-visible spectral changes over time for the reaction between photochemically generated Ru(bpy)₃³⁺ (0.10 mM, 1 equivalent) and **1** (0.10 mM). Using the absorbance at 828 nm, the lifetime of the oxidized **1** was fitted to a mono-exponential decay curve and τ_{828nm} was found to be 27 ± 4 mins. (b) Comparison of the UV-visible spectra of **1**, **1** + 1 eq. Ru(bpy)₃³⁺, and **1** + 2 eq. Ru(bpy)₃³⁺.

Figure 4.12 UV-visible spectral changes of **2** over time at applied potentials (with respect to platinum pseudo reference electrode) of (a) 1.0 V, (b) 1.4 V, and (c) 1.8 V, recorded at -80 °C in PrCN. The black arrows highlight the spectral changes at a particular applied potential. (d) Comparison of the UV-visible spectra recorded at different applied potentials and the spectrum before any potential had been applied.

Figure 4.13 (a) UV-visible spectra of **2** (0.10 mM, black), **2** + [Ar(Br)₂]₃N⁺SbF₆⁻ (< 0.10 mM, red), **2** + [Ar(Br)₂]₃N⁺SbF₆⁻ (< 0.20 mM, blue), **2** + [Ar(Br)₂]₃N⁺SbF₆⁻ (< 0.30 mM, grey), measured at -80 °C in PrCN. (b) UV-visible spectral changes over time of **2**³⁺ at -80 °C in PrCN. With reference to the absorption band at 585 nm, 8% of **2**³⁺ decayed within 60 minutes.

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Figure 4.15 Synthetic route of $[\text{Ar}(\text{Br})_2]_3\text{N}^+\text{SbF}_6^-$.

Figure 5.1 Reaction scheme of the desired photoactivation of **1** for dye degradation.

Figure 5.2 Mössbauer spectra of (a) 2 mM solution of $^{57}\text{1}$ in 1:1 $\text{H}_2\text{O}:\text{ACN}$, (b) 2 mM solution of $^{57}\text{1}$ in ACN, and (c) solid **1**. The black lines are the spectral simulations representing >95% of the absorption. The shaded areas are the spectral contributions from $^{57}\text{Fe}^{\text{III}}$ (black). A high-spin Fe^{III} impurity (5-10%) that we attribute to a deligated by-product, is observed in all cases. (d) Infrared spectra of **1** (black) and **1** after exchange with D_2O (red). Regions containing infrared bands of interest are marked with *. (e) Region containing O-D stretch (* in Figure 5.3d), with infrared signals from D_2O (blue). (f) Region containing O-H stretch (* in Figure 5.3d).

Figure 5.3 Photodegradation of MB with the following reagent concentrations: $[\text{Co}(\text{NH}_3)_5\text{Cl}_3] = 10\text{ mM}$, $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 0.020\text{ mM}$, $[\text{1}] = 0.60\text{ mM}$, and $[\text{MB}] = 0.60\text{ mM}$. (a) UV-vis absorption spectra of the photodegradation of MB without **1** (control). (b) UV-vis absorption spectra of the photodegradation of MB with **1**. (c) Comparison between MB photodegradation in the presence of **1** and the control without **1**.

Figure 5.4 Characterization data of **1-TAML-(Br)_n** generated from the reaction containing **1**, (ArMe)₃N^{•+} (4 eq), and tetraethylammonium bromide (TEABr, 10 eq). (a) Negative-ion ESI-MS of the crude reaction mixture 30 minutes after addition of the (ArMe)₃N^{•+} oxidant. The assigned intermediates are labelled. (b) Br 3d XPS data of **1-TAML-(Br)_n**. The fit (red, binding energy = 70.7 eV) represents the component completely attributable to aryl bromide. (c) ¹H NMR spectra of demetallated aliquots of the reaction mixture, withdrawn at time intervals 1 (red), 3 (blue), and 15 (green) minutes after addition of the (ArMe)₃N^{•+} oxidant. The spectrum of TAML before oxidation is shown in black. The dashed lines highlight the characteristic ¹H NMR signals from TAML (grey) and the proposed TAML-(Br)₂ (orange). The ¹H NMR signals (labelled as H_A, H_B, and H_C) are proposed to arise from the major TAML-(Br)₂ isomeric product, while the remaining signals (*) likely originate from another isomer of TAML-(Br)₂ with Br substitution at a different position of the aryl ring.

Figure 5.5 The ¹H NMR spectrum of the demetallated TAML-(Br)₂ ligand derived from acid hydrolysis of **1-TAML-(Br)₂**. The NMR signals assigned to the symmetrical TAML-(Br)₂ are marked with a red asterisk (*). The unassigned signals are proposed to be the asymmetrically bromide-substituted TAML-(Br)₂ or decomposed TAML-(Br)₂ during hydrolysis.

Figure 5.6 (a) Negative-ion ESI-MS of the crude reaction mixture containing **1** (1 eq), (ArMe)₃N^{•+} (4 eq), and TEACl (10 eq) 18 hours after addition of the (ArMe)₃N^{•+} oxidant. The assigned intermediates are shown. (b) Cl 2p XPS data. The fit (red) contains higher energy components (blue and green) assignable to aryl chloride, and lower energy components (grey and orange), corresponding to inorganic chloride ions. (c) ¹H NMR spectra of the demetallated aliquots of reaction mixture **1** (1 eq) + (ArMe)₃N^{•+} (4 eq) + TEACl (10 eq), withdrawn at time intervals 1 (red), 30 (blue), and 90 (green) minutes after addition of the

(ArMe)₃N^{•+} oxidant. The spectrum of TAML before oxidation is shown in black. The dashed lines highlight the characteristic ¹H NMR signals from TAML (grey). Due to the moderate conversions of TAML to TAML-(Cl) and TAML-(Cl)₂, based on the ESI-MS data, the ¹H NMR signals at different time points suggest slow reaction of the TAML, with small amounts of isomeric mixtures of TAML-(Cl) and TAML-(Cl)₂ as minor products.

Figure 5.7 (a) UV-vis spectrum of **1** (0.20 mM, black). UV-vis spectra of reaction mixtures of Br⁻ (10 eq) + **1** (red), and Cl⁻ (10 eq) + **1** (blue). The spectra of **1** in the presence of excess halide were measured at intervals of 3 minutes, and no further spectral changes were observed beyond 3 minutes. (b) UV-vis spectrum of **1** (0.20 mM, black) and the UV-vis spectral changes over time after the addition of CN⁻ (10 eq).

Figure 5.8 Possible mechanisms that could lead to the observed **1-TAML-(X)** products following the oxidation of **1-X**. The compounds marked in red arise from a second molecule of X⁻ or **1**, instead of the original **1-X** and its oxidized intermediates.

Figure 5.9 (a) ¹H NMR spectra of reaction mixture containing DMOB (1 eq), **1** (1 eq), and TEABr (10 eq), before (top), 5 minutes after (middle), and 24 hours after (bottom) the addition of (ArMe)₃N^{•+} (2 eq). The characteristic ¹H NMR signals from DMOB (blue dashed lines) and (ArMe)₃N (■) are labelled. The ¹H NMR signals marked by * originate from TAML-(Br)_n (Figure 5.6), formed from the demetallation of **1(Br)-TAML-(Br)_n**. Negative-ion ESI-MS of the reaction mixture of **1** (1 eq) + DMOB (1 eq) + Br⁻ (10 eq), before (b) and 5 minutes after (c) the addition of (ArMe)₃N^{•+} oxidant (2 eq). The assigned intermediates are labelled. The signals marked with * are assigned to TAML-(Br) (red), TAML-(Br)₂ (blue), and [TAML-(Br)₃] (orange).

Figure 5.10 (a) UV-visible spectral changes from the reaction between oxidized **1-Br** (0.20 mM) and TEABr (2.0 mM) in ACN. The inset shows the absorbance decay monitored at 893 nm (a characteristic band of the oxidized **1-Br**), and the solid red line shows the fit to the kinetics. (b) Plot of k_{obs} against Br^- concentration. The linear fit of the data gives a second-order rate constant, k , for the aromatic substitution of oxidized **1-Br**. Negative-ion ESI-MS of the reaction mixture of **1** (1 eq) + Cl^- (1 eq) + $(\text{ArMe})_3\text{N}^{\bullet+}$ oxidant (2 eq) before (c) and after (d) the addition of Br^- (10 eq). The signal marked with a red * is assigned to the demetallated TAML-(Br).

Figure 5.11 Mössbauer spectra of (a) $^{57}\text{1}$ and $\text{Ru}(\text{bpy})_3^{3+}$, (b) $^{57}\text{1}$, $\text{Ru}(\text{bpy})_3^{3+}$, and Br^- , (c) $^{57}\text{1}$, $\text{Ru}(\text{bpy})_3^{3+}$, and Cl^- , (d) $^{57}\text{1}^+-\text{(CN)}_2$. All $\text{Ru}(\text{bpy})_3^{3+}$ oxidant solutions were generated photochemically from $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ precursors to minimize interference from the exogenous anions. Samples (a) to (c) were taken 1 minute after the addition of the oxidant. The black lines are the simulations representing >95% of the absorption. Shaded areas are the spectral contributions from $^{57}\text{1-TAML}^{\bullet+}$ (blue) and $^{57}\text{1}^+$ (red). A high-spin Fe^{III} impurity (5-10%) that we attribute to a deligated by-product, is observed in all cases.

Figure 5.12 Proposed mechanism for the oxidation of **1**, followed by valence tautomerization between $\text{1(X)-TAML}^{\bullet+}$ and Fe^{IV} intermediates, depending on the exogenous anion.

Figure 5.13 (a) UV-vis spectrum of **1** (orange) and the UV-vis spectral changes over time upon oxidation of **1** by $(\text{ArMe})_3\text{N}^{\bullet+}$ (1.05 eq) in the presence of excess of CN^- (5 eq.). (b) The change in absorbance, monitored at 837 nm over time. The mono-exponential fit is the line in red, giving an estimated lifetime, $\tau_{837\text{nm}}$, of 4.4 ± 0.7 hours. Characterization data of the CN^- -stabilized 1^+ product generated from the reaction **1** + 5 eq. KCN + 1.05 eq. $(\text{ArMe})_3\text{N}^{\bullet+}$. (c) Negative-

ion CSI-MS and the assigned intermediates in the crude reaction mixture containing the dianionic (TAML)Fe^{IV} complex $[\mathbf{1}^+-(\text{CN})_2]^{2-}$. (d) Infrared spectra of KCN (black, $\nu_{\text{max}}/\text{cm}^{-1}$ 2076 (KCN)); $\mathbf{1} + 5$ eq. KCN (red, $\nu_{\text{max}}/\text{cm}^{-1}$ 2098 (Fe^{III}-CN)); and $\mathbf{1} + 5$ eq. KCN + 1.05 eq. (ArMe)₃N^{•+} (blue, $\nu_{\text{max}}/\text{cm}^{-1}$ 2127 (Fe^{IV}-CN)). (e) X-ray crystal structure of the dianionic Fe^{IV} TAML complex $[(\mathbf{1}^+-(\text{CN})_2)(\text{PPh}_4)_2]$, supporting an assignment of the Fe^{IV} valency by charge balance. Atom colors: gray for carbon, blue for nitrogen, red for oxygen, yellow for phosphorus, and orange for iron. The hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Fe1-C20 2.011(6), Fe1-C21 1.993(6), C20-N5 1.137(7), C21-N6 1.141(7). (d) UV-visible spectrum of a 0.62 mM purified $\mathbf{1}^+-(\text{CN})_2$ solution. $\lambda_{\text{max}}(\text{DCM})/\text{nm}$ 352 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1800), 452 (550), 596 (540), 639 (540), 728 (290), and 855 (160).

Figure 5.14 Reaction scheme depicting the syntheses of (ArMe)₃N and (ArMe)₃N^{•+}, and the oxidation of $\mathbf{1}$ by (ArMe)₃N^{•+} in the presence of different nucleophiles. Nu⁻: nucleophile.

Figure 6.1 Reaction scheme of the photoactivation of *g*-C₃N₄-**3** for pollutant degradation. The redox potentials of **3** featured in this figure are estimated from the CV of **2**.

Figure 6.2 (a) Adsorption isotherms of **3** loaded on *g*-C₃N₄. (b) Comparison of the diffuse reflectance spectra of **3** (black), *g*-C₃N₄ (red), and *g*-C₃N₄-**3** (blue). (c) Comparison of the IR spectra of **3** (black), *g*-C₃N₄ (red), and *g*-C₃N₄-**3** (blue). The grey dashed line features a unique IR band in **3** (1008 cm⁻¹) and this band is slightly blue-shifted in *g*-C₃N₄-**3** (1012 cm⁻¹, blue). (d) Fe K-edge XAS spectra of **3** (black), and *g*-C₃N₄-**3** (red). The inset shows the first derivative of the XAS spectra. The * marks the

pre-edge portion of the XAS spectrum. Fits of Fe K-edge EXAFS for (e) **3**, and (f) *g*-C₃N₄-**3**.

Figure 6.3 Photocatalytic degradation of *p*-cresol (0.10 mM, 20 mL) using *g*-C₃N₄-**3** (5.0 mg), with (a) O₂, and (b) NO₃⁻ as the sacrificial electron acceptor.

Figure 6.4 Cyclic voltammograms (scan rate = 0.1 V s⁻¹) of electrodes made of (a) FTO-*g*-C₃N₄ (black) and FTO-*g*-C₃N₄-**3** without annealing, (b) annealed FTO-*g*-C₃N₄ (black) and annealed FTO-*g*-C₃N₄ doped with **3**, (c) annealed FTO-*g*-C₃N₄ doped with **3** in the dark (black) and under irradiation (red). The inset shows the expanded potentials from 1.3 to 1.5 V to highlight the earlier onset potential brought about by irradiation of light. (d) Photoelectrochemical experiments of annealed FTO-*g*-C₃N₄ (black) and annealed FTO-*g*-C₃N₄ doped with **3** (red), measured at a fixed bias of 0.40 V. [Na₂SO₄] = 1.0 M.

Abbreviations

ACN	Acetonitrile
bpy	2,2'-Bipyridine
CSI-MS	Cold-Spray Ionization-Mass Spectrometry
DCM	Dichloromethane
DMF	<i>N,N</i> -Dimethylformamide
DMSO	Dimethyl Sulphoxide
DMOB	1,4-Dimethoxybenzene
EA	Ethyl Acetate
ESI-MS	Electrospray Ionization-Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
HPLC	High Performance Liquid Chromatography
<i>m/z</i>	Mass to Charge Ratio
NMR	Nuclear Magnetic Resonance
TAS	Transient Absorption Spectroscopy
TAML	Tetraamido Macrocyclic Ligand
THF	Tetrahydrofuran

Chapter 1

Introduction

This chapter entails the problem of the unmet energy demands in the modern society and the increasing environmental pollution as a result of energy derivation from the combustion of fossil fuels. Hence, utilizing solar energy to drive pollutant degradation is appealing. We hypothesize that we can incorporate existing catalysts capable of degrading pollutants into a photosensitizer through an anchoring group to facilitate the electron transfer between the irradiated photosensitizer and the catalyst. Subsequently, we will evaluate the pollutant degradation ability of this hybrid photosensitizer-catalyst system.

With this goal in mind, we defined the research scope and strategy for this project. This chapter is then concluded with a summary of the findings.

1.1 Hypothesis/Problem Statement

The modern society thrives from our ability to extract energy from Nature to fuel our energy demand. In particular, the derivation of heat energy from combustion of fossil fuels has propelled human civilization, especially during the industrial revolution. However, the rapid rate of release of carbon trapped in fossil fuels is not without its consequences, as evident from the ongoing climate change and increasing environmental pollution.¹ Water pollution is an emerging issue. Artificial compounds such as pharmaceuticals, illicit drugs, and personal care products have made their ways into our wastewaters. This poses a new challenge in the removal of these emerging contaminants because some of them cannot be degraded easily using our conventional water treatment system and they can bring about detrimental health effects to marine lives and to us.²

Solar energy is a sustainable and abundant energy resource. In Nature, photosynthesis is an important biochemical process to transform light energy into chemical energy. This process has been thoroughly investigated by the research community, and recent advancement in X-ray crystallography and various spectroscopic techniques has enabled better characterizations of the mechanisms of photosynthesis.³ This knowledge has led to the idea of artificial photosynthesis that promises a sustainable production of solar fuel.⁴ Very early on, Fujishima and Honda demonstrated an artificial model for photocatalytic water splitting using a titanium dioxide (TiO₂) photocatalyst.⁵ 45 year since this report was published, a lot of scientific progress in solar energy research has been made, such as the development of dye-sensitized solar cells (DSSC),⁶ and dye-sensitized photoelectrosynthesis cells (DSPEC).⁷

Similarly, remarkable progress has been made in the elucidation of the structures of other biological enzymes and how they are activated, with cytochrome P450 being one of the examples.⁸ This catalyst is able derive chemical energy from O₂

oxidant to form the highly reactive oxoiron(IV)-porphyrin radical-cation, $(\text{Porp}\bullet^+)\text{Fe}^{\text{IV}}(\text{O})$ (Compound I; Porp = porphyrin), capable of driving challenging biological oxidations.⁹ As a result, numerous biomimetic high valent heme and non-heme catalysts have been developed to emulate this type of catalyst.¹⁰ Among these catalysts, tetraamido macrocyclic ligand (TAML) iron complexes, $(\text{TAML})\text{Fe}$, are exceptionally efficient at water pollutant degradation.¹¹ More importantly, these pollutant degradation reactions can be done in aqueous environment using H_2O_2 as a green oxidant, earning $(\text{TAML})\text{Fe}$ complexes a place in the pulp bleaching sector.¹²

$(\text{TAML})\text{Fe}^{\text{III}}$ complexes, upon oxidized by two electrons, forms a highly reactive $(\text{TAML})\text{Fe}^{\text{V}}(\text{O})$ intermediate,¹³ which is able to degrade dyes, chlorophenols,^{11a,14} nitrobenzenes,^{11b,15}, transfer O-atom,^{14a} and activate strong C-H bonds.¹⁶ We hypothesize that the oxidation of $(\text{TAML})\text{Fe}$ complexes can also be achieved photochemically. Several strategies, ranging from direct photoexcitation of a $(\text{TAML})\text{Fe}$ complex, to energy or charge transfer from an excited photosensitizer to a $(\text{TAML})\text{Fe}$ complex, have been considered. In the latter case, an anchoring group connecting the $(\text{TAML})\text{Fe}$ complex to the photosensitizer may improve the charge transfer rate.

1.2 Objectives and Scope

The objective of this research project is to oxidize (TAML)Fe complexes photochemically and subsequently use the reactive high valent (TAML)Fe intermediates to perform pollutant degradation. The initial phase of the project involved the selection of a suitable (TAML)Fe complex from the literature that fits our envisioned photocatalytic system. Apart from its degradation capability, factors such as operational stability at neutral pH, and feasibility of introducing anchoring groups into the synthetic route, were considered as well. Then, the chosen (TAML)Fe complex was characterized using electrochemical techniques and spectroscopic measurements to probe its electrochemical and photophysical properties. These parameters were used to evaluate if the photochemically excited (TAML)Fe intermediate can perform pollutant degradation. In addition, we used this information to select suitable photosensitizers for the photochemical activation of the (TAML)Fe complex. Then we assembled various photocatalyst system and checked its performance at photocatalytic pollutant degradation. Both homogeneous and heterogeneous hybrid TAML(Fe)-light absorbing semiconductor material photocatalyst systems were considered.

1.3 Dissertation Overview

This thesis describes the utilization of light energy to drive pollutant degradation catalyzed by (TAML)Fe catalysts.

Chapter 1 highlights the problems that this research project aims to tackle. The research objectives and scope are also described.

Chapter 2 reviews published works on several topics, including (i) photosensitizers, (ii) biomimetic catalysts for oxidation reactions, (iii) tetraamido macrocyclic ligand (TAML)Fe complexes, and (iv) photoactivation of catalysts. From this information, new questions are posed and subsequently how this PhD project aims to address these research gaps.

Chapter 3 discusses the syntheses of various (TAML)Fe complexes in study, namely (TAML)Fe (**1**), (TAML-COOMe)Fe (**2**), and (TAML-COOH)Fe (**3**). Due to the limitation of commercially available precursors, a new synthetic route to obtain **2** and **3**, alongside the synthetic rationales and challenges are described. Characterizations of all the synthetic intermediates and final products are also presented.

Chapter 4 elaborates the electrochemical technique and spectroscopic measurements performed on **1** and **2** to characterize their electrochemical and photophysical properties. Apart from the results, the implications of these measurements, and how they shaped our research direction, are also highlighted. At the end of the chapter, characterizations of a formally Fe^{VI} (TAML)Fe complex are described. This chapter helps to rationalize the reaction conditions that were employed in the photocatalytic pollutant degradation in Chapters 5 and 6.

Chapter 5 begins with our attempt to degrade dyes using a homogeneous

photocatalyst system. The reaction did not result in dye degradation as we expected, instead ligand modification was observed. In our effort to elucidate the reasons for these unexpected results, we discovered that an anion-dependent valence tautomerization in (photo)chemically oxidized (TAML)Fe intermediate took place. Hence, this chapter is devoted to the product analysis and mechanism elucidation of this rarely reported phenomenon.

Chapter 6 depicts the anchoring of our carboxylate-functionalized (TAML-COOH)Fe (**3**) on graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) photosensitizer. This hybrid $g\text{-C}_3\text{N}_4$ -**3** heterogeneous photocatalyst system offers a possible solution to the problems encountered in the homogeneous system (Chapter 5). The results from the characterizations of the materials, photocatalytic experiments, and photoelectrochemical experiments are discussed in this chapter.

Chapter 7 recaps the findings from previous chapters and the new understanding about the photochemical activation of (TAML)Fe complexes. A thorough review of the overall work in the context of the thesis hypothesis is given. Finally, this chapter describes future work to extend our comprehension of the photochemical activation of (TAML)Fe complexes.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Establishing a new synthetic route for (TAML)Fe complexes synthesis, which widens the scope of precursors and increases the possibilities of synthesizing other functionalized (TAML)Fe complexes.
2. Characterizing the photophysical properties of (TAML)Fe complex in a $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system using nanosecond transient absorption spectroscopy (TAS).
3. Assessing and characterizing a possibly formally Fe^{VI} intermediate at low temperatures.
4. Reporting the phenomenon of anion-dependent valence tautomerization in a (photo)chemically oxidized (TAML)Fe complex.
5. Anchoring the (TAML-COOH)Fe complex on graphitic carbon nitride to make a heterogeneous hybrid photocatalyst.

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Chapter 2

Literature Review

This Chapter reviews reported works in literature. The review is separated into four subtopics: (i) photosensitizers, (ii) biomimetic catalysts for oxidation reactions, (iii) tetraamido macrocyclic ligand (TAML)Fe complexes, and (iv) photoactivation of catalysts. Based on the review, outstanding questions are identified. Subsequently, the PhD project is designed accordingly to address these research gaps.

2.1 Overview

In plants, photosynthesis is initiated when light absorbing units photosystem I (PS I) and photosystem II (PS II) in chlorophylls absorb sunlight, followed by the charge separation. The separated charges, electrons (e^-) and holes (h^+) are further separated by the electron transport chain to minimize recombination. The h^+ are transported to the oxygen evolving center (OEC) Mn_4Ca cluster, where h^+ are stored. Accumulation of four h^+ then oxidizes water to molecular oxygen.¹ On the other hand, e^- are transported to the enzyme $NADP^+$ (NADP = nicotinamide adenine dinucleotide phosphate) reductase that catalyzes the reduction of $NADP^+$ to NADPH. NADPH is an important energy storing cofactor that also protects cells against reactive oxygen species (Figure 2.1).² Energy is also derived from the electron transport chain, where adenosine diphosphate (ADP) nucleotide is phosphorylated to form the high energy adenosine triphosphate (ATP), Nature's energy storage unit.³ This complicated but elegant system of storing solar energy in the form of O_2 , an essential component for aerobic lifeforms, and in the form of NADPH and ATP, both of which are essential in the transformation of CO_2 into organic matters in plants.

Figure 2.1 Schematic representation of photosynthesis consisting of PS I and PS II light absorbing units, electron transport chain, oxygen evolving center, and NADP reductase.

Artificial photosynthesis strives to emulate natural photosynthesis by assembling materials or compounds that can perform specific functions of the natural

enzymes in natural photosynthesis. It is an appealing solution to our current reliance on unsustainable derivation of energy from fossil fuels combustion. Instead, we use the charges, obtained from light-induced charge separation, to perform redox reactions, thereby turning the redox products into solar fuel. To draw parallels between natural and artificial photosynthesis, a photosensitizer would assume the role of PS I and PS II, an oxidation catalyst would take the role of Mn_4Ca cluster at the OEC, a reductive catalyst would play the role of NADP^+ reductase enzyme, and finally the connection between the interfaces of these components would be the electron transport chain. Moreover, in artificial photosynthesis, we have the freedom of choosing and assembling the components according to our objectives. For example, to generate solar fuel, a highly efficient redox catalyst would be desirable; whereas for a solar cell, charge mobility of the photosensitizer should ideally be high.

We first identified and compared the reported photosensitizers to select the potential photosensitizers suitable for our artificial photosynthesis system. Then we investigated potential oxidative catalysts to be activated photochemically. Biomimetic oxidative catalysts are promising because they can be activated using environmentally friendly oxidants such as O_2 and H_2O_2 , and they also exhibit high potency in oxidation reactions, capable of performing challenging chemical transformations such as C-H activation. Hence we investigated the available biomimetic oxidative catalysts and their modes of activation. Through this process, we identified (TAML)Fe complexes to be our target oxidative catalyst. Subsequently, we studied the various generations of (TAML)Fe complexes and analyzed the reported means of activation of these complexes, including chemical, electrochemical, and photochemical activations. Since reports of photochemical activation of (TAML)Fe complexes are rare, we looked into reported photochemical activations of other metal complexes to explore possible ways to activate (TAML)Fe complexes photochemically.

2.1.1 Photosensitizers

Similar to natural photosynthesis, a photosensitizer (akin PS I and PS II) ideally should have a high extinction coefficient, a good charge separation, a physiochemical stability, and suitable excited photoredox potentials (for molecular photosensitizer) or band structure (for light absorbing semiconductor materials).

In the field of molecular photosensitizers, heavy transition metal complexes such as Ru^{II} , Pt^{II} , and Ir^{III} have been reported to be excellent photosensitizers due to the formation of triplet excited states. Coupled with proper ligand design to ensure that the separated charges are localized at different parts of the metal complex, these molecular photosensitizers can achieve exceptionally long lifetime,⁴ and this provides more time for the separated charges to be used for photoredox reactions. It is interesting to note that there is a lot of ongoing research on developing photosensitizers using Earth abundant d-block metals to overcome the costs of rare-earth metals.⁵ Apart from metal complexes, organic dyes are also good candidates as molecular photosensitizers.⁶ The photophysical and spectroscopic properties of molecular photosensitizers are well studied, and their (excited) redox potentials can be tuned by varying the ligand. However, the ligands and rare-earth metals cost generally more than the light absorbing semiconductor materials, and some of them require advanced synthetic skills in their syntheses.

On the other hand, there is a lot of progress on light-absorbing semiconductor research. They consist of metal oxides such as titanium dioxide (TiO_2), tungsten oxide (WO_3), bismuth vanadate (BiVO_4) etc., metal non oxides such as gallium arsenide (GaAs), cadmium selenide (CdSe), zinc sulfide (ZnS) etc., and non-metal semiconductors such as carbon nitride (C_3N_4), silicon (Si), silicon carbide (SiC).⁷ Inorganic-organic hybrid perovskites have also recently emerged as a new contender in the field of light absorbing materials.⁸ These materials are cheaper

and easier to synthesize compared to the molecular photosensitizers. However, being a less mature research area, there is still room for the study of their photophysical and spectroscopic properties. Some of these semiconductors are also sensitive to traps and the exact morphology may be difficult to reproduce.

A hybrid of molecular photosensitizer and semiconductor nanomaterials gained much attention when O'Regan and Grätzel first reported the dye-sensitized solar cell (DSSC), incorporating $\text{Ru}(\text{bpy})_3^{2+}$ onto colloidal TiO_2 films.⁹ This hybrid system takes advantage of $\text{Ru}(\text{bpy})_3^{2+}$ molecular photosensitizer's ability to absorb visible light, and the band structure of TiO_2 to generate photoelectricity. This concept was later developed into dye-sensitized photoelectrosynthesis cell (DSPEC), which produces solar fuels.¹⁰

In summary, some of the aforementioned photosensitizers will be considered for the photochemical activation of (TAML)Fe complexes. We will use a molecular photosensitizer in our homogeneous photochemical system, and light absorbing semiconductor materials in our heterogeneous rendition.

2.1.2 Biomimetic Catalysts for Oxidation Reactions

High-valent Fe oxo cofactors are key intermediates in carrying out important metabolic reactions such as hydroxylation, epoxidation, and electrophilic aromatic substitution.¹¹ Particularly, the heme-containing metalloenzyme, cytochrome P450, has generated enormous scientific interest. P450 can utilise O₂ to transform into a highly reactive oxo iron(IV)-porphyrin radical-cation, (Porp•⁺)Fe^{IV}(O) (Compound I; Porp = porphyrin), capable of driving challenging biological oxidations.¹² Efforts to understand Compound I have thus inspired many metalloporphyrin model compounds.¹³ Through these studies, (Porp•⁺)Fe^{IV}(O) is now recognised as the reactive species governing the rate-limiting hydrogen abstraction step to give (Porp)Fe^{IV}(OH) (Compound II).^{12a,14}

The redox non-innocent nature of the porphyrin facilitates the stabilisation of high valent Fe centres, as seen in Compound I, (Porp•⁺)Fe^{IV}(O), which is formally analogous to an Fe^V-oxo complex. In synthetic Mn porphyrinoid complexes, the ligand radical-cation form often exhibit higher reactivity compared to the Mn^V-oxo counterpart. For instance, Abu-Omar and co-workers reported a Mn corrole system, which tautomerises from (tpfc)Mn^V(O) (tpfc = 5,10,15-tris(pentafluorophenyl)corrole) to (tpfc•⁺)Mn^{IV}(OH) in the presence of an organic acid, and the latter form remarkably exhibits five orders of magnitude higher electron transfer reactivity.¹⁵ Similarly, Goldberg and co-workers reported an enhanced rate of C-H cleavage in the Lewis acid (LA)-induced Mn^{IV}(O-LA)(TBP8Cz•⁺) (TBP8Cz = octakis(*p*-*tert*-butylphenyl)corrolazinato³⁻).¹⁶

Concomitantly, non-heme Fe complexes bearing ligands such as tetraamido macrocyclic ligands (TAML),¹⁷ tripodal tris(carbene),¹⁸ tetracarbene macrocycle,¹⁹ N4Py,²⁰ and tetramethyl cyclam (TMC)²¹ have

also been investigated as bioinspired and biomimetic counterparts.²² These complexes have provided seminal insights to pivotal biochemical transformations using oxidants such as O₂ and H₂O₂.^{11a,23} These high valent non-heme Fe oxo complexes are potent enough to perform challenging C-H activation of alkanes.^{11d,24}

O₂ is an environmentally benign oxidant to generate high valent oxo iron intermediates, with H₂O being the by-product. Recently, many research groups have demonstrated that O₂ is able to oxidize non-heme Fe complexes, though this is usually coupled with electron rich substrates. For instance, oxidation of (TAML)Mn^{III} to (TAML)Mn^V(O) in the presence weak allylic C-H bonds was achieved using O₂ as the oxidant.²⁵ Likewise, a biuret-modified (TAML)Fe^{III}, activated by atmospheric O₂, has recently been shown to catalyse the epoxidation of alkenes.²⁶

Finally, while not commonly reported, there are reports describing the generation of high valent Fe oxo complexes by electrochemical means. Complex [Fe^{III}₂(μ-O)(tpenaH)₂]⁴⁺ (tpenaH = *N,N,N'*-tris(2-pyridylmethyl)ethylenediamine-*N'*-acetate) was oxidized to its [Fe^{IV}(O)(tpenaH)]²⁺ counterpart via electrolysis in an aqueous environment and this reactive intermediate was able to oxidize alcohols and alkanes.²⁷ Using electrolysis as the energy source to activate the Fe catalyst is becoming a more viable option when coupled with solar cells, since the development in solar cell research has been tremendous since the inception of DSSCs.²⁸

In summary, a search in the literature has shown that biomimetic catalysts possess promising potentials to perform challenging reactions such as alkane C-H activation. This finding aligns with our objective to degrade pollutants that often constitute persistent chemical bonds. Therefore, we

proceeded with choosing a suitable biomimetic catalyst as our catalyst for photocatalytic pollutant degradation.

2.1.3 Tetraamido Macrocyclic Ligand (TAML)Fe Complexes

Among the reported biomimetic metal complexes, (TAML)Fe system developed by Collins and coworkers stood out to us. This class of catalyst is such potent oxidants that they have been used for pulp bleaching, degradation of recalcitrant pollutants, water oxidation, and even the destruction of explosives in water.^{17,29} The most attractive feature of (TAML)Fe catalysts is that they are operational in aqueous environment, whereas most biomimetic metal complexes reported carried out their oxidation reactions in organic solvents such as ACN.³⁰

Typically, (TAML)Fe compounds are oxidized from Fe^{III} to transient higher valent Fe^{IV} and Fe^V(O) intermediates by hypervalent iodine compounds (PhIO), NaOCl, or H₂O₂, with the Fe^V(O) verified as the active species in the degradation of pollutants.^{17,29,31} Apart from chemical oxidants, the high valent oxo Fe intermediates can also be accessed using O₂.³² Although O₂ is only able to oxidize (TAML)Fe^{III} to the oxo Fe^{IV} counterpart, the oxo Fe^{IV} intermediate can disproportionate to form the Fe^{III} and Fe^V(O) intermediates in the right conditions, and subsequently the Fe^V(O) intermediate can be used for more interesting oxidation reactions.^{32b,32c} Furthermore, (TAML)Fe complexes can also be activated electrochemically without the use of chemical oxidants. In the report by Demeter *et al.*, electrocatalytic water oxidation was achieved by immobilizing a (TAML)Fe complex on a carbon electrode.³³ The divergence of (TAML)Fe catalysts activation from the use of chemical oxidants to greener methods such as using O₂ and electrochemical activation, shows the growing interests in the scientific community to propel the (TAML)Fe catalyst technology into practical applications.

Among the (TAML)Fe complexes that have been reported to exhibit pollutant degradation capability in aqueous environment (Figure 2.2), the 4th generation (TAML)Fe catalyst interested us since it was reported to perform best among the (TAML)Fe compounds for degrading methyl orange dye at neutral pH.³⁴ For simplicity purposes, the 4th generation (TAML)Fe complexes will be referred simply as (TAML)Fe complexes from Chapter 3 onwards, the term “1st generation” will be specified when the 1st generation (TAML)Fe complexes are referred, and the 5th generation (TAML)Fe complexes will be referred as (bTAML)Fe complexes (abbreviated from biuret-modified (TAML)Fe).

Figure 2.2 Overview of the various generations of (TAML)Fe complexes reported for water treatment. The axial ligand, Y is usually H₂O. Details on different X₁ and X₂ can be found in the report by Denardo *et. al.*³⁴

In summary, the activation mechanisms of (TAML)Fe complexes have been reviewed. The 4th generation (TAML)Fe complex has been chosen for this research project because of its operational stability in pH 7 aqueous conditions.

2.1.4 Photoactivation of Catalysts

One of the simplest ways to activate a catalyst photochemically would be to irradiate light directly on the catalyst. The excited catalyst would react with substrates, or electron donor or electron acceptor, which otherwise without light would have been unreactive towards the catalyst. Such ideal mode of photochemical activation of catalysts, however, is rare, due to the fast recombination of the MLCT-separated charges (MLCT = metal-ligand charge transfer) in transition metal complexes.³⁵ Nevertheless, exciting the ligand-to-[Fe^{IV}(O)] charge transfer using near UV light has been reported to activate N4Py Fe complexes.³⁶ Through careful ligand design, visible light can also be used to activate catalyst directly. One of these examples is a class oxo vanadium complexes that can perform selective C-C bond cleavage using visible light.³⁷

On the other hand, coupling the catalyst with a photosensitizer is another strategy to achieve photochemical activation, though a deeper understanding of the photophysics between the photosensitizer and the catalyst is required.³⁸ Hence, transient absorption spectroscopy is a useful tool to probe the charge transfer kinetics between the various components in this photocatalyst system.³⁹ Nam and Fukuzumi, have demonstrated that high valent (N4Py)Fe^{IV}(O) intermediates can be generated by two-electron oxidation via irradiating (N4Py)Fe^{II} in the presence of Ru(bpy)₃²⁺ and sacrificial oxidants.⁴⁰ They have also applied this concept in the asymmetric epoxidation of terminal olefins via photocatalytic oxidation of the chiral manganese catalyst, (*R,R*-BQCN)Mn^{II}(OTf)₂ (BQCN = N,N-

dimethyl-N,N-bis(8-quinolyl)cyclohexane-diamine; OTf = CF₃SO₃).⁴¹ In addition, Panda *et al.* have shown photochemical water oxidation by (bTAML)Fe^{III} catalysts with Ru(bpy)₃²⁺ as the photosensitizer, via the intermediacy of (TAML)Fe^V(O).⁴²

The choice of photosensitizers extends beyond molecular photosensitizers, since light absorbing semiconductor materials have experienced a tremendous growth in variations and mechanistic understandings. Doping these semiconductor materials with catalysts provides a cost effective way to perform photoredox catalyses, given the ease of upscaling and low cost of manufacturing of these materials.⁴³ This concept is the operating principle behind photoelectrosynthesis cell (DSPEC). Numerous reports have been published using photoelectrocatalysis with semiconductor materials: water oxidation,⁴⁴ proton reduction, CO₂ reduction, just to name a few.⁴⁵

In summary, photochemical activation of a catalyst can be achieved via the direct irradiation of the catalyst, and pairing the catalyst with a photosensitizer. Both of these activation modes will be applied in this research project.

2.2 Research Gap

As described in section 2.1.3, recent research efforts have aimed to develop the (TAML)Fe-catalyzed water treatment system into a more cost effective and a more environmental friendly system, by using green oxidants such as O_2 . This effort has also been seen in the electrocatalytic activation of the Fe catalyst, where the electrical energy can be harvested from solar cells such as DSSCs.

Recently, reports on photochemical activation of (bTAML)Fe complexes to perform water oxidation,⁴⁶ and epoxidation,⁴⁷ have opened up a new avenue for the activation of (TAML)Fe complexes. On closer examination, we realized that only the first electron oxidation from the (bTAML)Fe^{III} to the (bTAML)₂Fe^{IV}(μ -O) dimer was done by the photochemically oxidized photosensitizer, namely Ru(bpy)₃³⁺. To generate the (bTAML)Fe^V(O) reactive intermediate, a stronger persulfate anion radical ($SO_4\bullet^-$) oxidant was required,⁴⁶ implying that the Ru(bpy)₃³⁺ is not a strong enough oxidant to oxidize the Fe^{IV}(O) intermediate to the Fe^V(O) intermediate. Similarly, in the absence of $SO_4\bullet^-$, achieved by replacing the $S_2O_4^{2-}$ with Co(NH₃)₅Cl₃ electron acceptor, the (bTAML)₂Fe^{IV}(μ -O) dimer disproportionates to form the (bTAML)Fe^V(O) reactive intermediate and the (bTAML)Fe^{III} precursor (Figure 2.3).⁴⁷⁻⁴⁸ However, the proposed mechanism of the photochemical activation of (bTAML)Fe by Ru(bpy)₃³⁺/Co(NH₃)₅Cl₃ was not substantiated with experimental evidence such as transient absorption spectroscopic measurements. Thus, we will conduct transient absorption spectroscopic measurements on the photoactivation of (TAML)Fe complexes using the Ru(bpy)₃³⁺/Co(NH₃)₅Cl₃ photosensitizer system.

Figure 2.3 Overview of the oxidation of (bTAML)Fe^{III} using photochemically generated Ru(bpy)₃³⁺ and the various reported ways to obtain (bTAML)Fe^V(O).

In addition, we are intrigued by the lack of reports on the photochemical activation of the 1st and 4th generations of (TAML)Fe complexes, especially when the 4th generation (TAML)Fe complexes have been reported to perform the best amongst all the six generations of the (TAML)Fe compounds at the degradation of methyl orange dye at pH 7.³⁴ Hence, we would like to investigate the photochemical activation of the 4th generation (TAML)Fe complex by characterizing its electrochemical and photophysical properties.

In summary, the research progress on (TAML)Fe complexes has shown tremendous potential to move from the more conventional but less appealing for upscaling chemical oxidants to more cost effective and environmental friendly activation methods. However, reports on photochemical activation of (TAML)Fe complexes are rare and its activation mechanisms have not been thoroughly elucidated. In addition, these reports featured only the photochemical activation of (bTAML)Fe complex and those of other generations of (TAML)Fe complexes remain unreported. Therefore, this research project aims to explore these areas to understand the photochemical oxidation of (TAML)Fe complexes and apply this knowledge to systematically design a photocatalyst assembly that will perform pollutant degradation..

2.3 Ph.D. in the Context of Literature

Having identified the research gaps in literature, we defined the scope of the Ph.D. project accordingly. Firstly, we intend to use transient absorption spectroscopic experiments to study the photophysics of the photoactivation of (TAML)Fe complexes using the $\text{Ru}(\text{bpy})_3^{3+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system. This is also coupled with electrochemical characterization of the (TAML)Fe complexes to evaluate if the scope of photosensitizers can be expanded beyond $\text{Ru}(\text{bpy})_3^{2+}$.

We also propose that using photosensitizers that give stronger oxidized intermediates or oxidizing excited intermediates may be able to oxidize (TAML)Fe^{III} to the (TAML)Fe^V(O) complexes directly. Reports of such photosensitizers can be found in the literature. Excited $\text{Ru}(\text{bpz})_3^{2+}$ (bpz = 2,2'-bipyrazine) has been reported to perform chloride oxidation.⁴⁹ Acridinium dyes also have strongly oxidizing excited intermediates, capable of catalyzing nucleophilic aromatic substitutions.⁵⁰ Alternatively, light absorbing semiconductor materials that possess suitable band structures will also be considered.

After performing all the characterizations, we will choose a suitable photosensitizer system and perform photocatalytic pollutant degradation in a homogeneous system (all components will be in solution phase) using this assembly. Subsequently, we will introduce anchoring groups on (TAML)Fe complexes to anchor onto semiconductor photosensitizers. This photosensitizer-(TAML)Fe complex hybrid has been reported to improve charge transfer kinetics and reduce recombination of the separated charges.⁵¹ Such assembly will enable heterogeneous photocatalytic pollutant degradation, and possibly minimize deactivation pathways of the anchored (TAML)Fe complexes.⁵²

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Chapter 3

Synthesis of (TAML)Fe Complexes

This chapter describes the syntheses of the (TAML)Fe complexes that have been investigated in this thesis. While the synthesis of (TAML)Fe (1) was adapted and modified from reported procedures, the syntheses of (TAML-COOMe)Fe (2) and (TAML-COOH)Fe (3) are novel. The synthetic principles and challenges following this new synthetic route will be discussed. Our new synthetic route enables the use of nitroanilines, whose range of commercially available derivatives is greater than that of phenylenediamines. We believe that this new approach would open new avenues to synthesize a greater variety of (TAML)Fe complexes that will aid in advancing our understanding of this family of Fe complexes.

3.1 Introduction

The same synthetic principle from published procedures has been applied in the syntheses of the (TAML)Fe complexes. Firstly, two (substituted) *o*-phenylenediamine precursors are condensed with two different acyl chloride moieties to form the TAML ligand, with the 13-member ring TAML ligand (compound **1D**, Figure 3.1) being the most common. Then, the (TAML)Fe complex is synthesized by reacting the deprotonated TAML ligand with an Fe^{II} salt (Figure 3.1).¹

Figure 3.1 Synthetic route of **1**.

Due to the limited options of commercially available *o*-phenylenediamine synthons for the TAML ligand containing a carboxylate (TAML-COOH) moiety, several attempts were made to functionalize *o*-phenylenediamine, so that the reported procedures can be applied. However, the lack of chemoselectivity in the functionalization of the aromatic aryl-H (Ar-H) bond hindered this strategy.

An alternative synthetic route was drafted to circumvent the lack of commercially available synthons. Nitroanilines are interesting because they are not only synthons of phenylenediamines, but there is also a wide range of commercially available derivatives of nitroanilines. Hence, we proposed a novel synthetic route for the TAML ligand, where the nitro group (compound **2B**, Figure 3.2) would

take the role of a *tert*-butyloxycarbonyl(Boc)-protected amine (compound **1B**, Figure 3.1), and the reduction of nitro to amine functional groups (compound **2B** to **2C**, Figure 3.2) would replace the existing Boc deprotection step (compound **1B** to **1C**, Figure 3.1).

Figure 3.2 Synthetic route of **2**.

The complex (TAML-COOMe)Fe (**2**) is a precursor of the intended complex (TAML-COOH)Fe (**3**), which will be anchored onto a photosensitizer for photocatalytic, oxidative reactions (Figure 3.3). However, **2** exhibits interesting properties, such as accessibility to a high valent oxidation state chemically and electrochemically, and resistance against nucleophilic substitution, which are not shown in **1**. Further investigations were carried out to understand these properties (Chapter 4).

Figure 3.3 Synthetic route of **3**.

3.2 Discussion

Esterification of 4-amino-3-nitrobenzoic acid was performed in accordance to a reported method.³ The workup described in the report implies a filtration of the reaction mixture suspended in MeOH. However, we realized that the product, **2A**, was mildly soluble in MeOH and some product would have been lost during the process of filtration. Hence, we changed the workup (section 3.6, synthesis of **2A**), because we thought that the authors might have conducted the filtration in water rather than in methanol, but did not mention it explicitly. Despite the changes to the workup, the yields from both our procedure and that described in the report are very similar.

Changing from a Boc-protected amine (**1A**) to a nitro group (**2A**) decreases the nucleophilic property of the adjacent aniline. Consequently, the reported procedure for the *N*-acylation of the aniline with dimethyl malonyl chloride did not work for the synthesis of **2B**, as it did for that of **2A**. A search in the literature revealed an interesting report by Phukan *et al.*, where molecular iodine (I₂) was found to promote *N*-acylation of amines under mild conditions, giving high selectivities and good yields.⁴ Inspired by this report, we attempted to use similar conditions and performed the acylation of **2A** at room temperature and under solvent-free conditions, but only a moderate yield of 44 % was obtained, based on ¹H NMR spectroscopic measurements. Further optimization of the method increased the isolated yield to 73% (section 3.6, synthesis of **2B**).

The reduction of **2B** to **2C** was synthetically challenging. Several reducing agents, including tin(II) chloride⁵ and zinc⁶ did not show promising results. Palladium on charcoal (Pd/C)-catalyzed hydrogenation, however, revealed the formation of some product **2C**, and was hence optimized. In our initial workup, after product **2C** was dissolved in DMF, filtered, and the filtrate collected, we removed the DMF *in vacuo* at 60 °C for 2 hours. We observed a change in the color of the

solution from pale green to orange, and the ^1H NMR signals became complicated. To further understand this change, the solution was heated for 7 hours, at which the signal corresponding to **2C** disappeared, based on a TLC analysis. The orange crude product was purified by recrystallization in MeOH and Et₂O mixture. Single crystals could not be successfully obtained for X-ray crystallography. Nevertheless, in another separate project, where the COOMe ester group was replaced with a diethyl phosphonate group and similar procedures were employed, orange crystals were obtained. Two different products were collected and analyzed by X-ray crystallography. The first type of crystals showed a structure containing benzimidazol-1-ol functionalities (Figure 3.4a). The second type of crystals revealed a structure containing benzimidazole groups (Figure 3.4b).

Figure 3.4 X-ray crystal structures containing (a) benzimidazol-1-ol, and (b) benzimidazole moieties. Atom colours: grey for carbon, blue for nitrogen, red for oxygen, and orange for phosphorus. The hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at 50% probability.

Having identified the products formed upon prolonged heating in DMF, we propose that intramolecular condensation is responsible for their formation. The amine groups in **2C** would attack the neighboring amide carbons, and subsequent elimination of water molecules would result in the benzimidazole products (right, Figure 3.5). Similarly, the benzimidazol-1-ol products can be explained by the intramolecular condensation of the partially reduced product of **2B** containing hydroxylamine groups instead of amine groups (left, Figure 3.5). To ensure the reduction of **2B** to **2C** is complete, we optimized the hydrogenation conditions to 10 atm H₂ for 36 hours, in contrast to the commonly reported conditions, namely 1 atm H₂ for a few hours. Despite various attempts to dissolve **2C** in more volatile solvents, **2C** was found to be only soluble in DMF. Therefore, we set the temperature to 30 °C *in vacuo* to remove most of the DMF, and obtained **2C** from precipitation of the resulting paste in water. Although ¹H and ¹³C NMR spectra of decent quality were obtained, elemental analyses of purified **2C** were not satisfactory, presumably due to the inevitable intramolecular condensation during the removal of DMF.

Figure 3.5 Proposed mechanism for the formations of benzimidazol-1-ol (left) and benzimidazole (right) products.

With the knowledge that **2C** can undergo intramolecular condensation, the synthesis of **2D** was performed at 0 °C instead of 25 °C. Finally, complex **2** was synthesized as reported by Ellis *et al.*^{1b} An X-ray crystallographic measurement of a single crystal of **2** reveals a square pyramidal structure, with water as the axial ligand (Figure 3.6). The Fe-N and Fe-O bond lengths are very similar compared to the (TAML(Cl)₄)Fe reported by Ellis *et al.*^{1b} It is also noteworthy to mention that similar crystal structures with water as the axial ligand were obtained using different solvent combinations (MeOH/Et₂O or THF/xylene) for recrystallization.

Figure 3.6 X-ray crystal structures of (a) the PPh₄ salt of **2**, supporting an assignment of the Fe^{III} valency by charge balance, and (b) **2** with the PPh₄ cation omitted for clarity. Atom colors: gray for carbon, blue for nitrogen, red for oxygen, yellow for phosphorus, and orange for iron. The hydrogen atoms, except for those attached to O9, have been omitted for clarity. The ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Fe1-O9 2.097(2), Fe1-N1 1.865(2), Fe1-N2 1.880(2), Fe1-N3 1.901(2), Fe1-N4 1.910(2).

Two strategies have been considered for the synthesis of **3**. The first approach involves the ester hydrolysis of **2D** (TAML-COOMe) to the corresponding carboxylic acid (TAML-COOH), followed by metallation to give complex **3**. Compound **2D** was hydrolyzed to TAML-COOH (the ¹H-NMR can be found in

Figure A.10 in Appendix) using the same method as that described for the synthesis of **3**. Reacting TAML-COOH with ferrous chloride (FeCl_2) via previously described methods did not give any indication of successful formation of the desired complex **3**, based on negative-ion mode ESI-MS analysis of the crude product. We propose that since the carboxylic acid protons are more acidic than the amide protons, the two additional negative charges from the deprotonated carboxylic acids will increase the pK_a of the four amide protons, thereby preventing complete deprotonation of the amide protons even when excess base is used, which is necessary for the insertion of Fe^{2+} ion.

While searching through the literature for possible solutions, we found a report by Khurana *et al.* that described a facile method to perform ester hydrolysis at ambient temperature.⁷ Motivated by their findings, we set out to optimize the conditions for the ester hydrolysis of complex **2** to form **3**. Through the analyses of the ESI-MS data of the crude reaction mixtures, we monitored the disappearance of **2** ($m/z = 534$) and the appearance of mass fragments corresponding to **3**. At temperatures 35 °C (Figure 3.7a) and 50 °C (Figure 3.7b), **2** remained as the major species (grey dashed line, Figure 3.7). Nonetheless, heating **2** at 70 °C for 2 hours showed that **2** had vanished and a new signal corresponding to (TAML-COOH)Fe ($m/z = 506$) had appeared (orange dashed line, Figure 3.7c). We believe that due to the anionic nature of **2**, nucleophilic attack on the ester carbonyl group by hydroxide anions (OH^-) may be impeded. However, heating the reaction mixture beyond the boiling point of MeOH increases the concentration of OH^- and consequently the rate of ester hydrolysis.

Figure 3.7 Negative-ion mode ESI-MS data of **2** hydrolyzed for 2 hours at various temperatures: (a) 35 °C, (b) 50 °C, and (c) 70 °C. The dashed lines represent principal ESI-MS signals from (TAML-COOMe)Fe (**2**, grey), and (TAML-COOH)Fe (**3**, orange).

Complex **3** dissolves very well in water, but not in most organic solvents, with the exception of MeOH, in which **3** exhibits mild solubility. In the presence of excess PPh_4^+ in water, the K^+ salt of **3** did not seem to have undergone cation exchange with PPh_4^+ to give a precipitate, unlike complexes **1** and **2**. Hence, the crude product was used for subsequent anchoring experiments without further purification. Attempts to grow single crystals of **3** for X-ray crystallography were also not successful, probably due to the inability to purify **3** via cationic exchange.

To gain more insights into the structure of **3**, we removed the Fe^{3+} metal center using a pH 7 phosphate buffer solution (using procedures in Chapter 5.2.6) and analyzed the demetallated ligand with ^1H NMR spectroscopy. Comparing the ^1H

NMR spectra of TAML-COOMe, **2D** (Figure 3.8a), TAML-COOH (from hydrolysis of **2D**, Figure 3.8b), and demetallated **3** (Figure 3.8c), the O-CH₃ methoxy ester protons are absent in TAML-COOH and demetallated **3** (grey dashed line, Figure 3.8), and the carboxylic acid COOH proton is present in TAML-COOH (orange dashed line, Figure 3.8), confirming the hydrolysis of the esters to carboxylic acids. The carboxylic acid COOH proton is not observed in demetallated **3** (orange dashed line, Figure 3.8c). We attribute this observation to the chelation by the carboxylate groups to K⁺ (from the phosphate buffer solution). Furthermore, we also believe that K⁺ (from the phosphate buffer solution) might have been trapped in the middle of the TAML-COO⁻ ligand (where Fe³⁺ was formally located), causing the amide protons to be slightly shifted downfield (green dashed line, Figure 3.8c).

The ¹H NMR spectrum of demetallated **3** shows that the ester hydrolysis of **3** was successful. In the absence of X-ray crystallography and reliable elemental analyses data, we tentatively assign **3** to be the tri-anionic K⁺ salt (right, Figure 3.3).

Figure 3.8 ^1H NMR spectra of (a) TAML-COOMe (**2D**), (b) TAML-COOH (from hydrolysis of **2D**), and (c) demetallated **3**. The dashed lines highlight the characteristic ^1H NMR signals from O-CH₃ methoxy ester protons (grey), carboxylic acid COOH proton (orange), and amide protons (green). The ^1H NMR signal marked with an * originates from H₃O⁺ (added as part of the procedure for the demetallation of TAML(Fe) complexes, Chapter 5.2.6). This broad signal is distinct from the ^1H NMR signal from O-CH₃ methoxy ester protons (grey dashed line).

3.3 Conclusion

In this chapter, the syntheses of the previously reported (TAML)Fe (**1**), a new (TAML-COOMe)Fe (**2**), and a new (TAML-COOH)Fe (**3**) have been described. Our synthetic approach utilizes nitroaniline precursors (right, Figure 3.9) instead of *o*-phenylenediamines (left, Figure 3.9), enabling access to a wider range of (TAML) ligand systems. The main challenge of this new synthetic route is the reduction of the nitro group (compound **2B**) to amine group (compound **2C**), where intramolecular condensation can occur to form the benzimidazole. Having discovered this side reaction, we optimized the experimental procedures accordingly, leading to success of synthesizing complex **2**. The novel complex **2** and its synthetic intermediates have been characterized using ¹H- and ¹³C-NMR spectroscopies, HR-MS, elemental analysis, and X-ray crystallography.

To introduce an anchoring group to the (TAML)Fe complex, the ester group in complex **2** was hydrolyzed to form complex **3** (bottom right, Figure 3.9). We found out that the hydrolysis of **2** required a higher concentration of KOH and a higher temperature than the described protocols. Complex **3** has been characterized using HR-MS, and its demetallated counterpart with ¹H-NMR spectroscopy. Purification of complex **3** is challenging because the complex shares very similar solubility with the MeOK salt produced during the hydrolysis reaction. As a result, elemental analysis and X-ray crystallography data are currently unavailable.

In the next chapter, the photophysical and electrochemical characterizations of complexes **1** and **2** will be discussed.

Figure 3.9 Schematic diagram comparing the reported synthetic route using *o*-phenylenediamine precursor (left) and the new synthetic route using nitroaniline precursor (right). The hydrolysis of **2** using KOH yields complex **3** (bottom right).

3.4 Materials and Methods

Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry (TCI). Unless otherwise stated, the commercial reagents were used as purchased. All reactions involving air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmospheres. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were used as received. The ^1H and ^{13}C NMR spectroscopic measurements were recorded on a JEOL ECA 400SL (400 MHz) or Bruker AV-500 (500 MHz) NMR spectrometer. The ^1H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield referenced to the residual protons of the deuterated solvents.

High-resolution mass spectra (HR-MS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Elemental analyses were performed with an Elementar vario MICRO cube analyzer.

3.5 Synthesis of (TAML)Fe (1)

The procedures were adopted and modified from both Ellis *et al.* and Sullivan *et al.*.^{1b,2} The synthetic route is illustrated in Figure 3.1.

***Tert*-butyl (2-aminophenyl)carbamate (1A)**

Compound 1,2-phenylenediamine (1.73 g, 16.0 mmol) was added to a three-neck round bottom flask connected to a dropping funnel and was dissolved in 75 mL anhydrous THF. Anhydrous Et₃N (1.8 mL, 15 mmol) was injected into the solution. Di-*tert*-butyl dicarbonate (Boc₂O, 3.32 g, 15.2 mmol) was dissolved in anhydrous THF (25 mL) and transferred into the dropping funnel. The Boc₂O solution was added dropwise into the 1,2-phenylenediamine solution and the reaction mixture was stirred overnight. The solvent was removed by rotary evaporation to give a viscous yellow liquid. The liquid was then suspended in pH 10 sodium bicarbonate solution (NaHCO₃; 50 mL) and extracted with DCM (3 x 50 mL). The organic fractions were combined and rinsed with saturated NaHCO₃ solution (100 mL). The combined organic fractions were dried over anhydrous sodium carbonate (Na₂CO₃) and filtered. The DCM was removed by rotary evaporation to yield a pale brown oil. The oil was recrystallized with CHCl₃/hexane at 4 °C to give colorless crystals of **1A** (1.49 g, 47%). ¹H NMR (DMSO-*d*₆, 500 MHz, Figure A.1 in Appendix): δ = 1.45 (s, 9 H, 'Bu), 4.80 (s, 2 H, NH₂), 6.52 (m, 1 H, ArH), 6.66 (m, 1 H, ArH), 6.82 (m, 1 H, ArH), 7.17 (m, 1 H, ArH), 8.26 (br, s, 1 H, CONHBoc) ppm. ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 28.1, 78.6, 115.7, 116.3, 123.7, 124.5, 124.9, 141.2, 153.6 ppm. HR-MS (ESI+, *m/z*) calculated for C₁₁H₁₇N₂O₂ [M + H]⁺ *m/z* = 209.1290, found 209.1282.

Di-*tert*-butyl (((2,2-dimethylmalonyl)bis(azanediyl))bis(2,1-phenylene))dicarbamate (1B)

Compound **1A** (1.49 g, 7.16 mmol) was added into a three-neck round bottom flask connected to a dropping funnel and was dissolved in anhydrous THF (36

mL), after which anhydrous Et_3N (1.05 mL, 7.52 mmol) was added. Dimethylmalonyl dichloride (0.50 mL, 3.8 mmol) was added to the dropping funnel containing anhydrous THF (36 mL). The flask was cooled to 0 °C. Dimethylmalonyl dichloride solution was added to the flask at a rate of 1 drop/second. After the addition was complete, the solution was warmed up to room temperature and stirred overnight. The chalky suspension was dried by rotary evaporation. The dried product was suspended in pH 10 Na_2CO_3 solution (30 mL) and extracted three times with DCM (30 mL each). The organic fractions were combined and rinsed with saturated NaHCO_3 solution (60 mL). The organic layer was dried over anhydrous Na_2CO_3 and filtered. The filtrate was dried by rotary evaporation and recrystallized in $\text{CHCl}_3/\text{Et}_2\text{O}$ to yield a white solid **1B** (1.25 g, 68%). ^1H NMR ($\text{DMSO}-d_6$, 500 MHz, Figure A.2 in Appendix): δ = 1.43 (s, 18 H, ^tBu), 1.56 (s, 6 H, CH_3), 7.11 - 7.17 (m, 4 H, ArH), 7.46 – 7.52 (m, 4 H, ArH), 8.70 (br, s, 2 H, CONH^tBoc), 9.28 (br, s, 2 H, CONH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 100 MHz): δ = 23.3, 28.0, 51.0, 79.5, 123.5, 124.1, 125.7, 126.1, 129.7, 131.7, 153.7, 172.1 ppm. HR-MS (ESI+, m/z) calculated for $\text{C}_{27}\text{H}_{37}\text{N}_4\text{O}_6$ $[\text{M} + \text{H}]^+$ m/z = 513.2713, found 513.2709.

***N*¹,*N*³-bis(2-aminophenyl)-2,2-dimethylmalonamide (1C)**

Compound **1B** (1.25 g, 2.44 mmol) was added into a round bottom flask connected to a dropping funnel and was dissolved in DCM (7.5 mL). Trifluoroacetic acid (TFA, 7.5 mL, 98 mmol) was added to the dropping funnel containing DCM (15 mL). The flask was cooled to 0 °C. TFA solution was added to the flask at a rate of 1 drop/second. After the addition was completed, the solution was warmed up to room temperature and stirred for two hours. The solvent of the resulting solution was removed by rotary evaporation to give a yellow oil. The oil was diluted with pH 10 Na_2CO_3 solution (20 mL) and extracted three times with DCM (20 mL each). The organic fractions were combined and rinsed with saturated NaHCO_3 solution (40 mL). The organic layer

was dried over anhydrous Na_2CO_3 and filtered. The filtrate was dried by rotary evaporation to give a white solid **1C** (0.555 g, 73%). ^1H NMR ($\text{DMSO}-d_6$, 500 MHz, Figure A.3 in Appendix): δ = 1.57 (s, 6 H, CH_3), 4.91 (br, s, 4 H, NH_2), 6.54 (m, 2 H, ArH), 6.71 (m, 2 H, ArH), 6.94 – 6.98 (m, 4 H, ArH), 9.00 (br, s, 2 H, CONH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 100 MHz): δ = 23.5, 50.7, 115.4, 115.9, 122.7, 126.9, 127.5, 144.1, 172.8 ppm. HR-MS (ESI+, m/z) calculated for $\text{C}_{17}\text{H}_{21}\text{N}_4\text{O}_2$ [$\text{M} + \text{H}$] $^+$ m/z = 313.1665, found 313.1663.

Compound 15,15-dimethyl-8,13-dihydro-5H-dibenzo[b,h][1,4,7,10]tetraazacyclotridecine-6,7,14,16 (15H,17H)-tetraone (1D)

Compound **1C** (0.490 g, 1.57 mmol) was added into a three-neck round bottom flask connected to a dropping funnel and was dissolved in anhydrous THF (770 mL). Oxalyl chloride solution (0.87 mL of a 2 M solution, 1.7 mmol) was injected into the anhydrous THF (175 mL) in the dropping funnel. Anhydrous Et_3N (0.46 mL, 3.3 mmol) was then added into the solution in the flask. The flask was cooled to 0 °C. Oxalyl chloride solution was added to the flask at a rate of 1 drop/second. After the addition was complete, the cloudy solution was warmed up to room temperature and stirred overnight. Removal of the solvent by rotary evaporation gave a pale yellow solid. The solid was suspended in deionized water (100 mL) and sonicated before being filtered off. The residue was washed with copious amounts of deionized water and then sonicated in Et_2O . The resulting residue was dried *in vacuo* to give a white solid **1D** (0.489 g, 85%). ^1H NMR ($\text{DMSO}-d_6$, 500 MHz, Figure A.4 in Appendix): δ = 1.55 (s, 6 H, CH_3), 7.27 – 7.37 (m, 6 H, ArH), 7.60 – 7.61 (m, 2 H, ArH), 9.54 (br, s, 2 H, CONH), 9.64 (br, s, 2 H, CONH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 100 MHz): δ = 23.3, 51.2, 125.5, 126.0, 126.5, 127.2, 130.8, 131.7, 161.9, 172.5 ppm. HR-MS (ESI-, m/z) calculated for $\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_4$ [$\text{M} - \text{H}$] $^-$ m/z = 365.1250, found 365.1258.

Sodium salt of 1

Compound **1D** (0.489 g, 1.33 mmol) was added into a Schlenk flask and was suspended in anhydrous THF (75 mL). NaH (60% in mineral oil, 0.234 g, 5.85 mmol) was subsequently added to the solution and the mixture was stirred vigorously for 15 minutes until the suspension turned pale yellow. Iron (II) chloride (0.211 g, 1.66 mmol) was added into the solution and the reaction mixture was stirred overnight, resulting in a brown-green suspension. Exposure of the solution to air caused the suspension to turn brown. The suspension was then filtered to give a dark brown filtrate and a dark brown residue, which were worked up separately to give two crops of product. The first crop was obtained by adding the filtrate into pentane (300 mL), giving rise to the formation of a brown precipitate. The precipitate was filtered off, dissolved in MeOH, and dried by rotary evaporation to give a reddish brown crystalline solid. The second crop was obtained by dissolving the residue in MeOH (3 x 5 mL) and filtered. The filtrate was collected and its solvent removed by rotary evaporation, giving a reddish brown crystalline solid. The combined yield from both crops was 0.513 g (84%). For cyclic voltammetric and transient absorption spectroscopic experiments, further purification using C-18 reverse-phase preparative column chromatography (Merck LiChroprep ®RP-18, 40 – 63 µm) was required. The Na salt of **1** (0.100 g) was dissolved in 3 mL of ultrapure water and introduced into the column. The orange band observed was eluted with 25% MeOH in ultrapure water. The column should be completed within an hour to minimize degradation of the Na salt of **1** in the column. Alternatively, cation metathesis could also be performed on the Na salt of **1** to form the PPh₄ salt as the purification step. HR-MS (ESI-, *m/z*) calculated for C₁₉H₁₄FeN₄NaO₄⁻ *m/z* = 418.0364, found 418.0362.

PPh₄ salt of 1

The Na salt of **1** (0.100 g, 0.229 mmol) was dissolved in ultrapure water (10 mL) to give a red solution. Tetraphenylphosphonium chloride (PPh₄Cl, 0.412 g, 1.10 mmol) was added as a solid into the solution and sonicated for 30 seconds,

resulting in an orange suspension. The suspension was filtered and the residue was rinsed with ultrapure water (30 mL). The residue was then dissolved in MeOH and dried by rotary evaporation to give a reddish brown solid.

3.6 Synthesis of (TAML-COOMe)Fe (2)

The synthetic route is illustrated in Figure 3.2.

Methyl 4-amino-3-nitrobenzoate (2A)

Compound 4-amino-3-nitrobenzoic acid (3.64 g, 20.0 mmol) was added to a two-neck round bottom flask connected to a dropping funnel and was dissolved in anhydrous MeOH (42 mL). Thionyl chloride (SOCl₂, 20 mL of a 1 M solution, 20 mmol) was transferred into the dropping funnel. The SOCl₂ solution was added dropwise into the 4-amino-3-nitrobenzoic acid solution over 30 minutes and the reaction mixture was heated under reflux overnight after the complete addition of SOCl₂. The solvent was removed by rotary evaporation to give a yellow solid. The solid was then suspended in a pH 10 Na₂CO₃ solution (80 mL) and filtered. The residue was washed with water (40 mL) and filtered. The residue was subsequently dried *in vacuo* to give a yellow powder of **2A** (4.0 g, 98%). ¹H NMR (DMSO-*d*₆, 400 MHz, Figure A.5 in Appendix): δ = 3.79 (s, 3 H, CH₃), 7.03 (d, *J* = 8.8 Hz, 1 H, ArH), 7.81 (dd, *J* = 2.0, 8.8 Hz, 1 H, ArH), 7.96 (s, 2 H, NH₂), 8.50 (d, *J* = 2.0 Hz, 1 H, ArH) ppm. ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 49.4, 100.8, 103.4, 110.3, 111.6, 115.7, 127.0, 139.8 ppm. HR-MS (ESI+, *m/z*) calculated for C₈H₉N₂O₄ [M + H]⁺ *m/z* = 197.0562, found 197.0570. Elemental analyses for C₈H₈N₂O₄ calculated: C, 48.98; H, 4.11; N, 14.28%; found: C, 48.99; H, 4.51; N, 14.00%.

Dimethyl 4,4'-((2,2-dimethylmalonyl)bis(azanediyl)) bis(3-nitrobenzoate) (2B)

Compound **2A** (2.85 g, 14.5 mmol) was added into a two-neck round bottom flask and was dissolved in anhydrous ACN (25 mL). Dimethylmalonyl dichloride (1.0 mL, 7.3 mmol) and iodine (184 mg, 0.127 mmol) were added into the reaction mixture. The reaction mixture was heated to 70 °C and stirred overnight. The solvent was then removed by rotary evaporation. The residue obtained was

purified by flash column chromatography (silica gel, hexane:ethyl acetate = 2:3). The yellow residue was further purified by recrystallization (hexane:EA = 1:9), yielding pale yellow crystals **2B** (2.6 g, 73%). ^1H NMR (DMSO- d_6 , 400 MHz, Figure A.6 in Appendix): δ = 1.60 (s, 6 H, CCH₃), 3.89 (s, 6 H, OCH₃), 8.14 (d, J = 8.4 Hz, 2 H, ArH), 8.27 (dd, J = 2.0, 8.4 Hz, 2 H, ArH), 8.49 (d, J = 2.0 Hz, 2 H, ArH), 10.57 (s, 2 H, NH) ppm. ^{13}C NMR (DMSO- d_6 , 100 MHz): δ = 22.6, 52.0, 52.7, 125.0, 125.7, 126.1, 134.5, 135.8, 140.3, 164.2, 171.0 ppm. HR-MS (ESI-, m/z) calculated for C₂₁H₂₀ClN₄O₁₀ [$M + \text{Cl}$]⁻ m/z = 523.0868, found 523.0866. Elemental analyses for C₂₁H₂₀N₄O₁₀ calculated: C, 51.64; H, 4.13; N 11.47%; found: C, 51.62; H, 4.55; N, 11.29%.

Dimethyl 4,4'-(2,2-dimethylmalonyl)bis(azanediyl) bis(3-aminobenzoate) (2C)

Compound **2B** (0.49 g, 1.0 mmol) was dissolved in EA (10 mL) and transferred into a vial. Subsequently, 10% palladium on carbon (Pd/C, 24 mg) was added to the solution. Hydrogen gas (10 atm) was introduced to the hydrogenation pressure vessel containing the vial and the reaction mixture was stirred at room temperature for 36 hours. The resulting crude product was filtered through Celite and the residue was washed with EA (10 mL) and MeOH (2 mL). The grey residue was then dissolved in DMF (5 mL) to give a dark green solution, which was filtered. The filtrate was further passed through a 0.2 μm filter to remove any remaining Pd/C. The filtrate was then dried at 30 °C *in vacuo* to obtain a green paste. The paste was suspended in deionized water (25 mL), sonicated, and filtered. The residue was washed with deionized water (30 mL) and dried *in vacuo* to give a pale green powder **2C** (0.38 g, 90%). The product was found to undergo a slow intramolecular condensation in solution. Hence, elemental analysis data of the product is not available and the product is used as prepared for the next step. ^1H NMR (DMSO- d_6 , 400 MHz, Figure A.7 in Appendix): δ = 1.58 (s, 6 H, CCH₃), 3.80 (s, 6 H, OCH₃), 5.18 (s, 4 H, ArNH₂), 7.15 - 7.20 (m, 4 H, ArH), 7.39 (d, J = 1.2 Hz, 2 H, ArH), 9.19 (s, 2 H, CONH) ppm. ^{13}C NMR

(DMSO-*d*₆, 100 MHz): δ = 23.5, 51.1, 51.9, 116.3, 116.9, 127.0, 127.3, 127.7, 143.6, 166.4, 172.7 ppm. HR-MS (ESI-, *m/z*) calculated for C₂₁H₂₄ClN₄O₆ [M + Cl]⁻ *m/z* = 463.1384, found 463.1383.

Dimethyl 15,15-dimethyl-6,7,14,16-tetraoxo-6,7,8,13,14,15,16,17-octahydro-5H-dibenzo [b,h][1,4,7,10]tetraazacyclotridecine-3,10-dicarboxylate (2D)

Compound **2C** (0.28 g, 0.66 mmol) was added into a three-neck round bottom flask that was connected to a dropping funnel and was dissolved in anhydrous THF (330 mL). Oxalyl chloride solution (0.81 mL of a 2 M solution, 1.6 mmol) was injected into anhydrous THF (65 mL) in the dropping funnel. Anhydrous Et₃N (0.51 mL, 3.7 mmol) was then added into the solution in the flask. The flask was cooled to 0 °C. The oxalyl chloride solution was added to the flask at a rate of 1 drop/second. After the addition was complete, the cloudy solution was warmed up to room temperature and stirred overnight. Removal of the solvent by rotary evaporation gave a pale yellow solid. The solid was suspended in deionized water (100 mL) and sonicated before being filtered off. The residue was washed with copious amounts of deionized water and then sonicated in Et₂O. The resulting residue was dried *in vacuo* to give a grey solid **2D** (0.20 g, 65%). ¹H NMR (DMSO-*d*₆, 400 MHz, Figure A.8 in Appendix): δ = 1.55 (s, 6 H, CCH₃), 3.88 (s, 6 H, OCH₃), 7.58 (d, *J* = 8.8 Hz, 2 H, ArH), 7.90 (d, *J* = 8.8 Hz, 2 H, ArH), 8.10 (s, 2 H, ArH), 9.90 (s, 2 H, CONH), 10.0 (s, 2 H, CONH). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 26.8, 48.8, 49.8, 109.3, 109.4, 109.6, 109.7, 112.9, 116.7, 137.6, 140.2, 145.7 ppm. HR-MS (ESI-, *m/z*) calculated for C₂₃H₂₁N₄O₈ [M - H]⁻ *m/z* = 481.1359, found 481.1354. Elemental analyses for C₂₃H₂₁N₄O₈·2 H₂O calculated: C, 53.28; H, 5.05; N 10.81%; found: C, 53.67; H, 5.32; N, 10.42%.

Sodium salt of 2

Compound **2D** (0.37 g, 0.76 mmol) was added into a Schlenk flask and was suspended in anhydrous THF (130 mL). NaH (60% in mineral oil, 0.13 mg, 3.3

mmol) was subsequently added to the solution and the mixture was stirred vigorously for 15 minutes until the suspension turned to pale yellow. Iron (II) chloride (0.12 g, 0.95 mmol) was added into the solution and the reaction mixture was stirred overnight, resulting in a brown suspension. The suspension was then filtered to give a dark brown filtrate and a dark brown residue, which were worked up separately to give two crops of product. The first crop was obtained by adding the filtrate into pentane (300 mL), giving rise to the formation of brown precipitate. The precipitate was filtered off, dissolved in MeOH, and dried by rotary evaporation to give a reddish brown crystalline solid. The second crop was obtained by suspending the residue in MeOH (3 x 5 mL) and filtered. The filtrate was collected and its solvent removed by rotary evaporation, giving a reddish brown crystalline solid. The combined yield from both crops was 0.32 g (78%). HR-MS (ESI-, m/z) calculated for $C_{23}H_{18}FeN_4O_8^-$ $m/z = 534.0474$, found 534.0477. Elemental analyses for $C_{23}H_{18}FeN_4O_8 \cdot Na^+ \cdot 3 MeOH$ calculated: C, 47.80; H, 4.63; N 8.58%; found: C, 47.58; H, 4.64; N, 8.52%.

PPh₄ salt of **2**

The Na salt of **2** (0.10 g, 0.19 mmol) was dissolved in ultrapure water (10 mL) to give a red solution. Tetraphenylphosphonium chloride (PPh₄Cl, 0.35 g, 0.95 mmol) was added as a solid into the solution and sonicated for 30 seconds, resulting in an orange suspension. The suspension was filtered and the residue was rinsed with ultrapure water (30 mL). The residue was then dissolved in MeOH and dried by rotary evaporation to give a reddish brown crystalline solid. Single crystals of the PPh₄ salt of **2** were grown by slow evaporation of a 1:1 MeOH:H₂O solution of **2** (0.020 g in 2 mL). The crystallographic data can be found Tables A.1-A.7 in Appendix.

3.7 Synthesis of (TAML-COOH)Fe (**3**)

The synthetic route is illustrated in Figure 3.3.

Potassium salt of **3**

A solution of potassium hydroxide (KOH, 0.16 g) in anhydrous MeOH (2.4 mL) was prepared and added to a reaction tube containing **2** (0.40 g, 0.70 mmol). The red solution was heated to 70 °C and stirred for 2 hours, giving a thick, brown suspension. The suspension was filtered and the residue was washed with MeOH (3 x 1 mL). The filtrate was collected and its solvent removed *in vacuo*, resulting in a hygroscopic green powder **3** (0.38 g, ~85%). The crude product **3** was used for anchoring onto photosensitizers without further purification. Complex **3** was demetallated (using procedures in Chapter 5.2.6) and the remaining solution was examined with ¹H NMR spectroscopy. ¹H NMR (DMSO-*d*₆, 500 MHz, Figure A.9 in Appendix): δ = 1.59 (s, 6 H, CCH₃), 7.48 (d, *J* = 8.5 Hz, 2 H, ArH), 7.82 (dd, *J* = 8.5, 1.5 Hz, 2 H, ArH), 8.18 (d, *J* = 1.5 Hz, 2 H, ArH), 10.12 (s, 2 H, CONH), 10.14 (s, 2H, CONH).

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Chapter 4

Characterization of (TAML)Fe Complexes

*This chapter describes the electrochemical and photophysical characterizations of (TAML)Fe complexes **1** and **2**. Techniques such as cyclic voltammetry and transient absorption spectroscopy have been employed for this purpose. These characterization techniques provide pivotal insights into the understanding of whether (TAML)Fe complexes can be photochemically activated, and if so, the mechanisms that are involved.*

*Through our studies, we discovered that three-electron oxidation of (TAML)Fe complexes may be possible. Therefore we performed chemical and electrochemical oxidations on **2**. Characterization and reactivity studies of the three-electron oxidized complex is still ongoing and some salient results are described in this chapter.*

*Main findings in this chapter are published as: J. H. Lim,; X. Engelmann,; S. Corby,; R. Ganguly,; K. Ray,; H. S. Soo, C-H activation and nucleophilic substitution in a photochemically generated high valent iron complex, *Chem. Sci.*, **2018**, accepted. DOI: 10.1039/C7SC05378A*

4.1 Introduction

Typically, (TAML)Fe catalysts are activated using chemical oxidants such as H_2O_2 to form the reactive (TAML)Fe^V(O) intermediates, which are responsible for the various degradation reactions reported.¹ Photochemical activation of (TAML)Fe using $\text{Ru}(\text{bpy})_3^{2+}$ as the photosensitizer has been reported for the biuret-modified (TAML)Fe, but studies on the mechanisms of the photoactivation have not been reported.² Furthermore, we are intrigued by the lack of reports of the photoactivation of other (TAML)Fe catalysts, some of which display higher reactivity towards bleaching Orange II dye when activated with H_2O_2 .³ Therefore, we set out to characterize the electrochemical and photophysical properties of **1** (the best performing (TAML)Fe catalyst at bleaching of Orange II dye at pH 7).³ The electrochemical properties of our new (TAML)Fe complex **2** were also characterized.

Cyclic voltammetry is a common electrochemical technique to probe the electrochemical properties of compounds. In cyclic voltammetry, an external bias is typically swept from the open junction potential (range of applied potential that does not cause any redox reaction in the analyte and consequently no Faradaic current is measured) to potentials where electrochemical reaction(s) takes place. This is followed by a reverse scan where the reverse electrochemical reaction would take place. Interpretation of the current recorded during this process gives information about the electrochemical properties of the analyte.⁴

Each redox couple can be categorized into reversible, quasi-reversible, and irreversible. Upon electron transfer (ET), there exists a time gap, within which the oxidized or reduced analyte can undergo other non-electron transfer-related (non-ET) reactions and consequently can be transformed into other products. During the reverse scan, the reacted analyte does not

undergo the reverse ET reaction at the same redox potential, thereby giving a lower measured current. When the non-ET reaction rate is much higher than the scan rate, v , then the redox wave appears irreversible, and vice versa. Therefore, varying the scan rate will provide information on the non-ET reaction rate as well.

Using cyclic voltammetry, we set out to determine the potentials at which oxidations of **1** and **2** occur. These potentials will aid in choosing suitable photosensitizers. Furthermore, the stabilities of the oxidized complexes can be estimated from the reversibilities of the redox waves.

Transient absorption spectroscopy (TAS) is a spectroscopic technique that monitors the changes in the spectral features of an analyte upon irradiation by a laser pulse. In principle, the laser pulse is set to a wavelength appropriate to excite the photosensitizer in study. Upon excitation of the photosensitizer, a probe records the spectral information at specified time intervals. Analysis of the spectral changes over time gives kinetics information about the excited photosensitizer. In the presence of other components, the reaction of the excited photosensitizer with the other components can also be studied.⁵

From the CV results, we have ascertained that $\text{Ru}(\text{bpy})_3^{2+}$ should be a suitable photosensitizer to oxidize complex **1**. Hence, we performed TAS to verify if **1** can be photochemically oxidized under partially aqueous conditions, while concurrently characterizing the absorption features of the oxidized **1** intermediates. These TAS studies of **1** in a homogenous system may help us to understand the photoactivation of **3** anchored onto a photosensitizer in a heterogeneous system in the future.

From the analysis of the cyclic voltammetry data of **1** and **2**, we got intrigued by the possibility of accessing a three-electron oxidized (TAML)Fe complex. Very recently, Nam *et al.* reported a (TAML•⁺)Fe^V-imido (formally Fe^{VI}) complex, which displayed a ~17,000 times higher nitrene transfer reaction rate compared to the (TAML)Fe^V-imido counterpart.⁶ Therefore, we attempted to oxidize **2** by three electrons. We did not perform a similar reaction on **1** because the CV data of **1** showed that oxidized **1** is less stable than oxidized **2**, and we had shown that the TAML ligand of oxidized **1** was susceptible to nucleophilic attack (Chapter 5). We also believe that using an outer-sphere oxidant such as Ru(bpy)₃³⁺, arylinium radical cation, or direct electrolysis is paramount to achieving TAML radical cation, (TAML•⁺)Fe (Chapter 5). Hence, we studied the oxidation of **2** chemically and electrochemically at low temperatures (e.g. -80 °C).

4.2 Results and Discussion

4.2.1 Cyclic Voltammetry

The cyclic voltammetric features of **1** show three quasi-reversible oxidations at $E_{1/2}$ potentials of +0.10, +0.39, and +0.63 V vs. Fc^+/Fc and irreversible reductions at -0.13 and +0.15 V (Figure 4.1a), as opposed to the single quasi-reversible wave at +0.50 V reported by Sullivan *et. al.*¹⁰ In all subsequent discussions, the potentials are reported relative to Fc^+/Fc . We propose that the experiments in the prior study may have been affected by the deposition of oxidized product(s) of **1** on the electrode, which we overcame by polishing the electrode after every potential sweep.

The irreversible reduction at -0.13 V appeared only if **1** had not been oxidized beyond +0.10 V (blue, Figure 4.1a). Similarly, the irreversible reduction at +0.15 V appeared only after **1** had been oxidized up to at least +0.39 V (red, Figure 4.1a). We believe that the oxidized **1** intermediates had undergone non-ET reactions, and these products gave rise to the new irreversible reduction peaks. Increasing the scan rates, ν (0.1 – 1.6 V s^{-1}) did not cause any significant change to the irreversible reduction peaks, suggesting that these non-ET reactions rates are too fast to be affected by our chosen range of scan rates.

On the other hand, the cyclic voltammogram of **2** reveals one irreversible oxidation at $E_{1/2} = 0.02$ V, and two quasi-reversible oxidations at $E_{1/2}$ potentials = +0.25 and +0.55 V (Figure 4.1b). Similar to the cyclic voltammogram of **1**, scanning beyond the second oxidation at +0.25 V resulted in a new irreversible reduction peak at 0.00 V (red, Figure 4.1b). However, the first oxidation wave of **2** seems irreversible, despite varying ν (0.1 – 5.0 V s^{-1}). We reconciled these results with different non-ET reactions taking place in the oxidized intermediates of **2**. It is noteworthy to mention that the peak shapes of **2** look more reversible

than those of **1**, especially in the third oxidation peak (black, Figure 4.1), implying that the three-electron oxidized **2** may exhibit more stability.

Figure 4.1 Cyclic voltammograms of Na salts of (a) **1** and (b) **2** over several scan ranges. [**1**] = 0.90 mM, [**2**] = 1.0 mM, [*n*-Bu₄NPF₆] = 100 mM, glassy carbon working electrode. Scan rate = 0.1 V s⁻¹.

From the CV measurements of **1** and **2**, both oxidized complexes exhibit some non-ET reactions, which may cause catalyst modifications when they are oxidized photochemically. Nonetheless, analysis of the peak shapes suggests that the high valent intermediate of **2** may be more stable than the high valent intermediate of **1**. We also noted that the potentials of oxidized **2** were slightly lower than those of **1**. This observation is counterintuitive, since **2**, having two electron-withdrawing ester substituents, should exhibit more positive reduction potentials. Therefore, more studies such as DFT calculations will be needed to understand this observation.

Most importantly, the CV experiments have shown that the oxidations of **1** and **2** by Ru(bpy)₃²⁺ ($E_{\text{Ru(III)/Ru(II)}} \approx +0.85 \text{ V}$)¹¹ should be thermodynamically feasible. Since **1** has been reported as the best (TAML)Fe oxidant at pH 7,³ we would like to activate **1** photochemically and then compare its reactivity with the reported reactivity. Therefore, Ru(bpy)₃²⁺ was chosen as the photosensitizer to study the kinetics of the photochemical oxidation of **1**.

4.2.2 Transient Absorption Spectroscopic (TAS) Studies

The expected elementary steps following the laser excitation of $\text{Ru}(\text{bpy})_3^{2+}$ are illustrated in Figure 4.2.

Figure 4.2 Anticipated elementary steps involved after laser excitation of $\text{Ru}(\text{bpy})_3^{2+}$.

We probed the characteristic wavelengths (at 365, 470, and 730 nm in absorbance mode, and 600 nm in emission mode) of the photochemically excited $\text{Ru}(\text{bpy})_3^{2+*}$ to observe the fate of $\text{Ru}(\text{bpy})_3^{2+}$ upon irradiation with 450 nm laser pulses. Some salient results are summarized in Figures 4.3 – 4.6 and Table 4.1.

Figure 4.3 TAS signals (black), probed at 365 nm, under different conditions depicted in Table 4.1. The fits to the kinetics are the lines in red. (a) Ru(bpy)₃Cl₂ only (Entry 1). (b) Ru(bpy)₃Cl₂ + **1** (Entry 2). (c) Ru(bpy)₃Cl₂ + Co(NH₃)₅Cl₃ (Entry 3). (d) Ru(bpy)₃Cl₂ + **1** + Co(NH₃)₅Cl₃ (Entry 4).

Figure 4.4 TAS signals (black), probed at 470 nm, under different conditions depicted in Table 4.1. The fits to the kinetics are the lines in red. (a) Ru(bpy)₃Cl₂ only (Entry 1). (b) Ru(bpy)₃Cl₂ + **1** (Entry 2). (c) Ru(bpy)₃Cl₂ + Co(NH₃)₅Cl₃ (Entry 3). (d) Ru(bpy)₃Cl₂ + **1** + Co(NH₃)₅Cl₃ (Entry 4).

Figure 4.5 TAS signals (black), probed at 730 nm, under different conditions depicted in Table 4.1. The fits to the kinetics are the lines in red. (a) Ru(bpy)₃Cl₂ only (Entry 1). (b) Ru(bpy)₃Cl₂ + **1** (Entry 2). (c) Ru(bpy)₃Cl₂ + Co(NH₃)₅Cl₃ (Entry 3). (d) Ru(bpy)₃Cl₂ + **1** + Co(NH₃)₅Cl₃ (Entry 4).

Figure 4.6 Transient *emission* spectroscopic signals (black), probed at 600 nm, under different conditions depicted in Table 4.1. The fits to the kinetics are the lines in red. (a) Ru(bpy)₃Cl₂ only (Entry 1). (b) Ru(bpy)₃Cl₂ + **1** (Entry 2). (c) Ru(bpy)₃Cl₂ + Co(NH₃)₅Cl₃ (Entry 3). (d) Ru(bpy)₃Cl₂ + **1** + Co(NH₃)₅Cl₃ (Entry 4).

Table 4.1 Summary of the lifetimes from the fits to the kinetics data in Fig. 4.3 – 4.6.

Entry	Lifetimes recorded at different probing wavelengths (ns)			
	365 nm ^a	470 nm ^a	730 nm ^a	600 nm ^b
1 ^c	660 ± 20	620 ± 20	640 ± 20	680 ± 30
2 ^d	540 ± 20	530 ± 20	570 ± 20	530 ± 20
3 ^e	390 ± 20	380 ± 20	400 ± 20	390 ± 20
4 ^f	$\tau_1 = 360 \pm 20$ $\tau_2 = 3010 \pm 150$	$\tau_1 = 390 \pm 20$ $\tau_2 = 2840 \pm 110$	$\tau_1 = 370 \pm 220$ $\tau_2 = 3020 \pm 120$	360 ± 20

^aTransient absorption signal. ^bTransient emission signal. ^cRu(bpy)₃Cl₂ (0.020 mM) only.^dRu(bpy)₃Cl₂ (0.020 mM) + **1** (0.20 mM). ^eRu(bpy)₃Cl₂ (0.020 mM) + Co(NH₃)₅Cl₃ (10 mM). ^fRu(bpy)₃Cl₂ (0.020 mM) + **1** (0.20 mM) + Co(NH₃)₅Cl₃ (10 mM). ^{c-f}

In the absence of any quencher, Ru(bpy)₃^{2+*} decays back to the ground state and has a photoluminescence band ($\lambda_{\text{max}} = 600$ nm) with a rate constant k_a (Figure 4.6a). The bimolecular quenching rate constant, k_b , is related to the lifetime, τ_b , of Ru(bpy)₃^{2+*} in the presence of **1** as the quencher (Figure 4.6b) with a concentration of [**1**], by the Stern-Volmer equation:

$$\frac{\tau_a}{\tau_b} = 1 + k_b \tau_a [\mathbf{1}]$$

where τ_a is the lifetime of Ru(bpy)₃^{2+*} in the absence of a quencher.

Photoemission lifetime at 600 nm is chosen as the reference wavelength, since it is characteristic of only Ru(bpy)₃^{2+*}, and is therefore free from interference from other species. The bimolecular quenching rate constant k_b was obtained by plotting τ_a/τ_b against [**1**] with a fixed vertical intercept of 1 (Figure 4.7a). The gradient ($k_b \tau_a$) was determined to be $3.6 \pm 0.1 \times 10^3 \text{ M}^{-1}$. Given that τ_a is 680 ± 30 ns (Figure 4.6a), k_b was subsequently calculated to be $5.3 \pm 0.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Since Ru(bpy)₃³⁺ is a long-lived species, the Stern-Volmer equation can be simplified to:

$$\frac{1}{\tau_d} \approx k_d[\mathbf{1}]$$

where τ_d is the lifetime of $\text{Ru}(\text{bpy})_3^{3+}$ in the presence of $\mathbf{1}$, and k_d is the corresponding bimolecular hole transfer rate constant from $\text{Ru}(\text{bpy})_3^{3+}$ to $\mathbf{1}$.

As $[\mathbf{1}]$ increases, the rate of consumption of $\text{Ru}(\text{bpy})_3^{3+}$ increases, resulting in a shorter lifetime τ_d . The wavelength 365 nm is chosen as the reference wavelength because at this wavelength $\text{Ru}(\text{bpy})_3^{3+}$ has a negative ΔOD whereas $\mathbf{1}^+$ has a positive ΔOD , compared to the ground state $\text{Ru}(\text{bpy})_3^{2+}$, thereby giving clear indication of the hole transfer from $\text{Ru}(\text{bpy})_3^{3+}$ to $\mathbf{1}$ (Figure 4.3d). From the bi-exponential fit of the transient spectroscopic signal, the longer lifetime, corresponding to the hole transfer from $\text{Ru}(\text{bpy})_3^{3+}$ to $\mathbf{1}$, was taken to be τ_d . A graph of $1/\tau_d$ against $[\mathbf{1}]$ was then plotted, with its vertical intercept set at 0 (Figure 4.7b). The gradient representing k_d , was found to be $3.9 \pm 0.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.

Figure 4.7 (a) Stern-Volmer plot for the quenching of the transient emission signal of $\text{Ru}(\text{bpy})_3^{2+*}$ at 600 nm by varying $[\mathbf{1}]$. (b) Simplified Stern-Volmer plot for the quenching of the transient absorption signal of $\text{Ru}(\text{bpy})_3^{3+}$ at 350 nm by varying $[\mathbf{1}]$.

A control experiment with $\mathbf{1}$ alone showed that it did not exhibit any observable transient absorption signals upon laser excitation. Intriguingly, $\mathbf{1}$ partly quenched the excited state of $\text{Ru}(\text{bpy})_3^{2+*}$ (Table 4.1 entry 2, Figures 4.3b, 4.4b, 4.5b, 4.6b, and 4.8c-d) compared to a solution containing only $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (Table 4.1 entry

1, Figures 4.3a, 4.4a, 4.5a, and 4.6a), with a bimolecular rate constant of $5.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Figure 4.7a). Since no new spectral features were observed beyond the decay of $\text{Ru}(\text{bpy})_3^{2+*}$ (Figure 4.8d), we tentatively attributed the process to triplet energy transfer from $\text{Ru}(\text{bpy})_3^{2+*}$ to **1**, followed by a non-radiative decay of **1**^{*} back to its ground state. Nevertheless, as reported previously,¹² $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ oxidatively quenched $\text{Ru}(\text{bpy})_3^{2+*}$ at an even faster rate due to the high concentrations that we used (Table 4.1 entry 3, Figures 4.3c, 4.4c, 4.5c, and 4.6c), despite having a lower biomolecular rate constant of $1.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.

In the presence of **1** and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, the photoluminescence at 600 nm of $\text{Ru}(\text{bpy})_3^{2+*}$ decayed with the shortest lifetime, τ_1 (Table 4.1 entry 4), due to both energy transfer to **1** and oxidative quenching by $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (Figure 4.6). Concomitantly, a transient oxidized (TAML)Fe species with an absorption band around 365 nm and broad absorption between 450-850 nm (Figure 4.9b) was observed. A second new, longer-lived time constant, τ_2 , of around 3010 ns (Table 4.1 entry 4) was determined from the transient absorption signals attraction between the cationic $\text{Ru}(\text{bpy})_3^{3+}$ and the anionic **1** at 365 nm (Figure 4.3d), which we attribute to electron transfer from **1** to $\text{Ru}(\text{bpy})_3^{3+}$. $\text{Ru}(\text{bpy})_3^{3+}$ can oxidize **1**, which then absorbs at 365 nm (positive ΔOD , Figure 4.3d) at longer μs timescales after the Ru^{III} has transformed back to the $\text{Ru}(\text{bpy})_3^{2+}$ ground state. The oxidation of **1** by $\text{Ru}(\text{bpy})_3^{3+}$ occurs with a near diffusion-controlled bimolecular rate constant of $3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Figure 4.7b), likely due to electrostatic attraction between the cationic $\text{Ru}(\text{bpy})_3^{3+}$ and the anionic **1**.

Figure 4.8 TAS of $\text{Ru(bpy)}_3\text{Cl}_2$, $\text{Co(NH}_3)_5\text{Cl}_3$, and **1**, featuring spectral changes over time after laser excitation: (a) 0 – 10 μs , and (b) 0 - 10 μs with expanded vertical scale. The squares (■) highlight absorption features of the transient oxidized **1**. TAS of $\text{Ru(bpy)}_3\text{Cl}_2$ and **1**, featuring spectral changes over time after laser excitation: (a) 0 – 10 μs , and (b) 0 - 10 μs with expanded vertical scale.

We also repeated TAS studies with longer timescales up to 4 seconds to investigate whether the spectral signals from oxidized **1** changed at a longer time scale. From the signals at 600 and 830 nm, the oxidized **1** did not decay in 4 seconds (Figure 4.9).

Figure 4.9 TAS signals of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.020 mM) + **1** (0.20 mM) + $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ (10 mM), on 4-second timescales with a (a) 600 nm probe wavelength, and a (b) 830 nm probe wavelength. The data recorded at both wavelengths show that the oxidized **1** has increased absorbance compared to **1**, and the lifetime of the oxidized **1** exceeds four seconds.

Using transient absorption spectroscopy, we have identified that photoexcited **1** does not have an observable lifetime in the nanosecond region. However, **1** was found to quench $\text{Ru}(\text{bpy})_3^{2+*}$ (red, Figure 4.10). The absence of newly formed species led us to propose that **1** quenches $\text{Ru}(\text{bpy})_3^{2+*}$ via energy transfer, and the photoexcited **1**^{*} transforms back to **1** through non-radiative decay. Nevertheless, when we generated $\text{Ru}(\text{bpy})_3^{3+}$ photochemically in the presence of a large excess of $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ (blue, Figure 4.10), we observed the oxidation **1** by $\text{Ru}(\text{bpy})_3^{3+}$ (green, Figure 4.10), forming a long-lived intermediate, with no sign of decay within 4 seconds.

Figure 4.10 Scheme summarizing the findings from TAS experiments.

Having ascertained that Ru(bpy)₃²⁺ photosensitizer is able to oxidize **1** photochemically, we proceeded to oxidize **1** using independently generated Ru(bpy)₃³⁺ and check if the oxidized **1** from TAS experiments is the same as that from chemical oxidation.

4.2.3 Chemical Oxidation of **1** Using Independently Generated Ru(bpy)₃³⁺

The resulting steady-state UV-visible spectra are shown in Figure 4.11. The spectral features of **1** + 2 eq. Ru(bpy)₃³⁺ are similar to those of **1** + 1 eq. Ru(bpy)₃³⁺ (Figure 4.11b), suggesting that the additional one equivalent of Ru(bpy)₃³⁺ was probably used to oxidize **1** and overcome the intrinsic decay of the oxidized form back to its reduced state during the measurement.

Figure 4.11 (a) UV-visible spectral changes over time for the reaction between photochemically generated $\text{Ru}(\text{bpy})_3^{3+}$ (0.10 mM, 1 equivalent) and **1** (0.10 mM). Using the absorbance at 828 nm, the lifetime of the oxidized **1** was fitted to a mono-exponential decay curve and $\tau_{828\text{nm}}$ was found to be 27 ± 4 mins. (b) Comparison of the UV-visible spectra of **1**, **1** + 1 eq. $\text{Ru}(\text{bpy})_3^{3+}$, and **1** + 2 eq. $\text{Ru}(\text{bpy})_3^{3+}$.

The one-electron oxidized intermediate (red, Figure 4.11b) has a λ_{max} at 606 nm ($\epsilon_{606} \approx 1200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 828 nm ($\epsilon_{828} \approx 1700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), with an estimated lifetime, τ_{828} , of 27 ± 4 mins at room temperature (Figure 4.11a). With reference to the four-second TAS results, both photochemically oxidized **1** (Figure 4.9) and chemically oxidized **1** (red, Figure 4.11b) have similar characteristic wavelengths, suggesting that the stable steady-state intermediate is probably the oxidized **1**. Therefore, we have shown that **1** can be oxidized by at least one electron in our $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ system.

4.2.4 Three-Electron Chemical Oxidation of **2**

To obtain more spectral information about the three oxidized intermediates of **2** observed in CV experiments (Figure 4.1b), we performed spectroelectrochemical measurements on **2** at -80°C . This temperature was chosen because the reported $(\text{TAML})\text{Fe}^{\text{V}}(\text{O})$ exhibited satisfactory stability at -60°C and could be characterized spectroscopically,^{1a} and our proposed three-electron oxidized **2** ($\mathbf{2}^{3+}$, a formally Fe^{VI} intermediate) may display a lower stability compared to $(\text{TAML})\text{Fe}^{\text{V}}(\text{O})$.

Firstly, spectral changes were observed when a potential of 1.0 V (with reference to the platinum pseudo reference electrode) was applied. An overall increase in absorbance over time in the range of 400 – 1000 nm was recorded (from black to grey, Figure 4.12a). We tentatively assign this intermediate as the one-electron oxidized **2** (**2⁺**), which represents the (TAML-COOMe)Fe^{IV} and (TAML•⁺-COOMe)Fe^{III} intermediates (see Chapter 5 for assignments). Increasing the potential to 1.4 V brought about a new spectrum (grey, Figure 4.12b) with λ_{max} at 595 nm ($\epsilon_{595} \approx 5200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 870 nm ($\epsilon_{870} \approx 4700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). We assign this intermediate as the two-electron oxidized **2** (**2²⁺**). Most interestingly, at 1.8 V, a new intermediate (grey, Figure 4.12c) whose spectrum contained a λ_{max} at 585 nm ($\epsilon_{585} \approx 12000 \text{ dm}^3 \text{ mol}^{-1}$) was recorded. Similarly, we assign this intermediate as the three-electron oxidized **2** (**2³⁺**). The comparison between the spectra of **2**, **2⁺**, **2²⁺**, and **2³⁺** are featured in Figure 4.12d.

Apart from electrochemical oxidation of **2**, we also used chemical oxidation to study the high valent **2** complexes. Among the chemical oxidants with redox potentials $E^{\circ'} > +0.55 \text{ V}$ (third redox potential in the cyclic voltammogram of **2**, Figure 4.1b) that we screened, (ArBr)₃N•⁺ ($E^{\circ'} = +0.70 \text{ V}$ vs. Fc⁺/Fc),¹³ Ru(bpy)₃³⁺ ($E^{\circ'} = +0.85 \text{ V}$ vs. Fc⁺/Fc),¹¹ and [Ar(Br)₂]₃N•⁺ ($E^{\circ'} = +1.14 \text{ V}$ vs. Fc⁺/Fc),¹³ only [Ar(Br)₂]₃N•⁺ produced the oxidized intermediate with a 585 nm absorption band in UV-visible spectroscopic measurements. Subsequently, we chose [Ar(Br)₂]₃N•⁺ with SbF₆⁻ instead of the more commonly reported SbCl₆⁻ anion to ensure that Cl⁻ would not dissociate from SbCl₆⁻ and bind to the oxidized intermediate. We performed redox titration of **2** with successive addition of one equivalent of [Ar(Br)₂]₃N•⁺SbF₆⁻ and recorded the corresponding UV-visible spectrum. However, it has been reported that [Ar(Br)₂]₃N•⁺SbF₆⁻ decomposes gradually in solution, and some authors adopted procedures where excess [Ar(Br)₂]₃N•⁺SbF₆⁻ was used for the oxidation.^{8,14} Therefore, we have denoted that the amount of [Ar(Br)₂]₃N•⁺SbF₆⁻ used in the redox titration experiments was less than the intended amount (caption in Figure 4.13).

Figure 4.12 UV-visible spectral changes of **2** over time at applied potentials (with respect to platinum pseudo reference electrode) of (a) 1.0 V, (b) 1.4 V, and (c) 1.8 V, recorded at -80 °C in PrCN. The black arrows highlight the spectral changes at a particular applied potential. (d) Comparison of the UV-visible spectra recorded at different applied potentials and the spectrum before any potential had been applied.

Figure 4.13 (a) UV-visible spectra of **2** (0.10 mM, black), **2** + $[Ar(Br)_2]_3N^{\bullet+}SbF_6^-$ (< 0.10 mM, red), **2** + $[Ar(Br)_2]_3N^{\bullet+}SbF_6^-$ (< 0.20 mM, blue), **2** + $[Ar(Br)_2]_3N^{\bullet+}SbF_6^-$ (< 0.30 mM, grey), measured at -80 °C in PrCN. (b) UV-visible spectral changes over time of 2^{3+} at -80 °C in PrCN. With reference to the absorption band at 585 nm, 8% of 2^{3+} decayed within 60 minutes.

The UV-visible spectra of various oxidized intermediates of **2** generated by chemical oxidation (Figure 4.13a) and electrochemical oxidation (Figure 4.12d) show similarities in the absorption bands. In particular, we have shown that 2^{3+} (grey) can be generated using both methods. The intermediate 2^{3+} decayed by 8% within 60 minutes at $-80\text{ }^{\circ}\text{C}$ in PrCN. In comparison to the (TAML)Fe^V(O) reported by de Oliveira *et al.*, which decayed by 10% within 90 minutes, 2^{3+} is less stable despite having been cooled to a lower temperature. This suggests that 2^{3+} is less stable than the (TAML)Fe^V(O), providing further evidence that 2^{3+} could be higher valent than the Fe^V counterpart.

With the spectral information in hand, we compared them with other high valent Fe complexes bearing different TAML ligands. The 1st generation [(TAML)Fe^{IV}]₂O has a broad absorption spectrum at room temperature in DCM with λ_{max} at 542 nm ($\epsilon_{542} \approx 7500\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and 856 nm ($\epsilon_{856} \approx 5400\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$),¹⁵ while the (TAML)Fe^V(O) counterpart recorded at $-60\text{ }^{\circ}\text{C}$ in PrCN has λ_{max} at 445 nm ($\epsilon_{445} \approx 5400\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and 630 nm ($\epsilon_{630} \approx 4200\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).^{1a} Similar to the UV-visible spectrum of (TAML)Fe^V(O), that of biuret-modified (TAML)Fe^V(O) measured at room temperature in ACN contained absorption bands at 441 nm ($\epsilon_{441} \approx 4350\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and 613 nm ($\epsilon_{613} \approx 3420\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). Comparing the UV-visible spectra of 2^{+} and 2^{2+} with those reported, there is not a significant resemblance. Interestingly, the spectrum of 1st generation (TAML•⁺)Fe^V-imido (formally Fe^{VI}) complex exhibits an absorption band at 545 nm ($\epsilon_{545} \approx 10000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). Such high extinction coefficient ϵ has not been observed in the (TAML)Fe^{IV}- or (TAML)Fe^V-oxo complexes. Complex 2^{3+} in our experiment has an absorption band 585 nm with ϵ exceeding 10000 (Figure 4.12c) and resembles a (TAML•⁺)Fe^V valency. Other spectroscopic measurements to characterize 2^{3+} such as electron paramagnetic resonance (EPR), Mössbauer, and X-ray absorption spectroscopy are still in progress.

We proceeded to evaluate the reactivity of 2^{3+} through kinetics measurements of 2^{3+} reacting with *p*-substituted thioanisoles (*p*-XC₆H₄SMe), since similar studies have been performed using other (TAML)Fe catalysts at -40 °C, thereby allowing a direct comparison of the reactivity between 2^{3+} and other high valent (TAML)Fe complexes.^{6,16} At -40 °C, 2^{3+} decayed at faster rate of 13 % (Figure 4.14a) as compared to 8% at -80 °C (Figure 4.13b) within 60 minutes. By fitting the kinetics of the decrease in absorbance of the 585 nm band, the decay rate of 2^{3+} , k_{decay} at -40 °C was estimated to be $2.8 \times 10^{-4} \text{ s}^{-1}$ (Figure 4.14b). As preliminary reactions, we reacted 2^{3+} with *p*-XC₆H₄SMe (X = OMe, Me, NO₂) under pseudo first-order conditions ($[p\text{-XC}_6\text{H}_4\text{SMe}] > [2^{3+}]$ by 10 – 40 times). The kinetics data of electron-rich *p*-(OMe)C₆H₄SMe at each concentration fits well to a mono-exponential function (Figure 4.14c). However, as the electron density of *p*-XC₆H₄SMe decreases from X = OMe to Me to NO₂, the kinetics show larger deviations from the expected pseudo first-order kinetics, as evident from the poorer mono-exponential fits to the kinetics (Figures 4.14e and 4.14g). Similarly, poorer positive correlations were observed in the plots of k_{obs} against $[p\text{-XC}_6\text{H}_4\text{SMe}]$ with decreasing electron densities of *p*-XC₆H₄SMe (Figures 4.14d, 4.14f, and 4.14h). We propose that 2^{3+} underwent other competing reactions apart from *p*-XC₆H₄SMe oxidation, and this is more prominent when the rate of *p*-XC₆H₄SMe oxidation, k is slow. One of these competing reactions could be the natural decay of 2^{3+} , with k_{decay} ($2.8 \times 10^{-4} \text{ s}^{-1}$, Figure 4.14b) being only an order of magnitude slower than the k_{obs} of *p*-(Me)C₆H₄SMe ($8.2 \times 10^{-3} \text{ s}^{-1}$, Figure 4.14e), and k_{obs} of *p*-(NO₂)C₆H₄SMe ($4.9 \times 10^{-3} \text{ s}^{-1}$, Figure 4.14g). We are also considering the potential competing reaction of 2^{3+} with O₂ from air introduced during the process of *p*-XC₆H₄SMe injection. Efforts to optimize the procedures of kinetics measurements are ongoing. Once this is achieved, we will expand the substrate scope to C-H activation and electron transfer reactions. Nevertheless, the decrease in k with

decreasing electron density of p -XC₆H₄SMe indicates that the oxidation of p -XC₆H₄SMe by $\mathbf{2}^{3+}$ is electrophilic in nature, which is the case for many reported high valent Fe intermediates.¹⁷

GC-MS analysis of the reaction mixture revealed the corresponding sulfoxide (p -XC₆H₄S(O)Me) as the sole product. This suggests that either an O-atom-transfer (OAT) reaction from $\mathbf{2}^{3+}$ to p -XC₆H₄SMe, or an electron transfer reaction from $\mathbf{2}^{3+}$ to p -XC₆H₄SMe to give p -XC₆H₄MeS $\bullet^+$, had occurred.¹⁸ The intermediate C₆H₅MeS $\bullet^+$ has been reported to react with O₂ to give the sulfoxide product.¹⁹ Further spectroscopic characterizations of $\mathbf{2}^{3+}$ will provide insights to the reaction mechanism.

We compared our experimental k of p -(OMe)C₆H₄SMe oxidation with those reported for other high valent (TAML)Fe complexes, since p -(OMe)C₆H₄SMe resembled pseudo first-order kinetics the most. Our experimental k (490 M⁻¹ s⁻¹, Figure 4.14d) is lower than the OAT transfer to p -(OMe)C₆H₄SMe reported for 1st generation (TAML)Fe^V(O) (k = 9000 M⁻¹ s⁻¹),¹⁶ and also the nitrene transfer to p -(OMe)C₆H₄SMe reported for (TAML $\bullet^+$)Fe^V-imido (k = 2300 M⁻¹ s⁻¹),⁶ with all experiments performed at -40 °C. We are not certain if the lower reactivity towards p -(OMe)C₆H₄SMe oxidation observed is due to the inherent properties of $\mathbf{2}^{3+}$ or the inaccuracy of our kinetics experiments as a result of the presence of competing reactions. We are currently performing more spectroscopic measurements on $\mathbf{2}^{3+}$ and reviewing our experimental procedures for the kinetics experiments.

Figure 4.14 (a) UV-visible spectral changes over time of 2^{3+} at -40 °C in PrCN, and (b) the corresponding absorbance decay monitored at 585 nm (a characteristic band of 2^{3+}). Absorbance decays monitored at 585 nm of the reactions between 2^{3+} and p -XC₆H₄SMe (40 equivalents), X = (c) OMe, (e) Me, or (f) NO₂. The solid red line shows the fit to the kinetics. Plots of k_{obs} against [p -XC₆H₄SMe], X = (d) OMe, (f) Me, or (h) NO₂. Each linear fit of the data gives a second-order rate constant, k , for the oxidation of p -XC₆H₄SMe.

4.3 Conclusion

In this chapter, cyclic voltammetry experiments on **1** and **2** have shown that $\text{Ru}(\text{bpy})_3^{2+}$ should be a suitable photosensitizer to oxidize **1** and **2** photochemically. As a proof of concept that (TAML)Fe complexes can be photochemically activated, we characterized the photophysical properties of **1** (best performing H_2O_2 -activated (TAML)Fe catalyst for methyl orange II degradation) using transient absorption spectroscopic (TAS) experiments. The TAS results have verified that the $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system is able to oxidize **1** by at least one electron, producing a relatively long-lived oxidized **1** intermediate. This intermediate was corroborated using UV-visible spectroscopic measurements of **1** oxidized by independently generated $\text{Ru}(\text{bpy})_3^{3+}$. In the next chapter, the photocatalytic degradation of dyes using the $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system and **1**, and other new findings will be discussed.

On the other hand, motivated by the possibility of accessing the rarely reported three-electron oxidized **2** (formally Fe^{VI} complex), we oxidized **2** electrochemically and chemically at low temperature ($-80\text{ }^\circ\text{C}$). The preliminary results indicate that the three-electron oxidized **2** (2^{3+}) may have been generated, and efforts to characterize this intermediate spectroscopically and by X-ray crystallography are still ongoing. Preliminary kinetics experiments of the reactivity of 2^{3+} in the oxidation of *p*-substituted thioanisoles have shown the electrophilic nature of this reaction. However, the kinetics data of slower reactions have suggested that other competing reactions may have occurred during the kinetics measurements. Therefore, the experimental procedures are being examined, in hopes of obtaining more accurate kinetics data of the reactivity of 2^{3+} towards various substrates.

4.4 Materials and Methods

4.4.1 Cyclic Voltammetry

Cyclic voltammetric (CV) measurements were conducted using a Biologic SP-300 potentiostat with 0.10 M *n*-Bu₄NPF₆ as the electrolyte in anhydrous ACN. The *n*-Bu₄NPF₆ was purchased from Sigma-Aldrich and recrystallized in THF/pentane. A standard three-electrode electrochemical cell was used with a glassy-carbon working electrode (3 mm in diameter from BASi®), a Pt wire as the counter electrode, and another Pt wire as the pseudo-reference electrode. The working electrode was polished over 0.05 μm alumina (Allied High Tech Products Inc.) after every scan. The analyte solution was bubbled with Ar for 5 minutes prior to each CV measurement and a positive Ar flow was maintained throughout the experiment.

4.4.2 Transient Absorption Spectroscopy

The transient absorption spectroscopic (TAS) and transient emission spectroscopic (TES) measurements were performed using an Edinburgh Instruments model LP920 transient absorption spectrometer equipped with a pulsed Xe probe lamp in conjunction with a Nd:YAG laser (Continuum model Surelite II-10) as the excitation source. The laser pulse width is 5-8 ns and the repetition rate is 10 Hz. During TAS measurements, the pulses were synchronized with the LP920 system at a frequency of 1 Hz. The pulse energy used was between 4-5 mJ/pulse. In all our transient absorption spectra, the detected intensity of the transmitted signals are presented as a logarithm of the ratio of the light intensity from the probe beam *after* laser excitation to the intensity *before* laser excitation (ΔOD). Hence, ΔOD refers to the increased absorption (positive ΔOD) or reduced absorption/emission

(negative ΔOD) of the transient photoexcited species relative to the ground state.

Pentaamminechlorocobalt(III) chloride ($\text{Co}(\text{NH}_3)_5\text{Cl}_3$) was added to the sample solution as a solid. Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($\text{Ru}(\text{bpy})_3\text{Cl}_2$) was prepared as a 1.0 mM stock solution in a volumetric flask. The stock solution was stored in a refrigerator for a maximum period of one week. The Na salt of **1** was purified by reverse-phase column chromatography and used in all transient absorption measurements. Similarly, a 1.0 mM stock solution of **1** was prepared. A stock solution of **1** was freshly prepared every day, since its stability in ACN is moderate. The quality of **1** may affect the absolute lifetimes of the transient absorption measurements. Therefore, the same batch of **1** was used throughout the whole set of experiments.

The samples were added in the solid form or as stock solutions into a 3.5 mL quartz cuvette (LATECH™, Model: Q-204). Ultrapure water (H_2O , Milli-Q Advantage A10, $\text{TOC} \leq 5$ ppb) and ACN (HPLC grade) were added to make a final volume of 3.0 mL with a ratio of $\text{H}_2\text{O}:\text{ACN} = 3:1$. The cuvette was then fitted with a rubber septum and sealed using Parafilm M®. The cuvette was sonicated to ensure that the solution was homogeneous. Then with a needle fitted through the rubber septum as a gas outlet, argon (Ar) gas was bubbled through the solution for 5 minutes and its transient absorption properties were measured. The detailed composition of each set of experiment is depicted in Table 4.1.

Table 4.2 Different conditions tested using 3 mL solutions for transient absorption measurements.

Entry	Reagents (concentration)		
	Co(NH ₃) ₅ Cl ₃ (10 mM)	Ru(bpy) ₃ Cl ₂ (0.020 mM)	1 (0.20 mM)
1		✓	
2		✓	✓
3	✓	✓	
4	✓	✓	✓

Each set of data was fitted to a single exponential or biexponential function to obtain the time constant(s) for the transient absorption signal according to the following two equations respectively:

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1}$$

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1} + A_2 e^{-(t-\tau_0)/\tau_2}$$

The parameters y_0 , τ_0 , A_n , and τ_n were determined by a least-squares fitting procedure in Origin. The term y_0 corresponds to the vertical intercept at long lifetimes and indicates whether the signal decays to a ‘permanent’ bleach (negative y_0) or absorption (positive y_0). The term τ_0 is the delay time of the excitation pulse from the start of the probe measurement during each photoexcitation cycle. A_n is the change in optical density after irradiation for the n th exponential term and τ_n is the corresponding time constant.

The errors corresponding to the fits of the transient signal lifetimes were determined via the principle of error propagation by calculating the root-mean-square deviation from the sum of squares of the uncertainties in each measured value. For each time-resolved measurement, the associated uncertainties included the laser pulse duration, spectrometer time-resolution, mass of samples, and volumes of samples, for example. Hence,

the error of the transient signal lifetime, $\delta\tau$, was calculated according to the following equation:

$$\delta\tau = \tau \cdot \sqrt{\left(\frac{\delta\tau_a}{\tau_a}\right)^2 + \left(\frac{\delta\tau_b}{\tau_b}\right)^2 + \left(\frac{\delta m_k}{m_k}\right)^2 + \left(\frac{\delta V_n}{V_n}\right)^2}$$

where τ = transient signal lifetime; $\delta\tau_a$ = uncertainty of the laser pulse duration; $\delta\tau_b$ = uncertainty of the spectrometer time-resolution; δm_k = uncertainty of the mass of k^{th} component, where k represents the different dissolved constituents such as $\text{Ru}(\text{bpy})_3\text{Cl}_2$, **1**, and $\text{Co}(\text{NH}_3)_5\text{Cl}_3$; δV_n = uncertainty of the n^{th} volume measurement, where n represents the n different volume measurements including stock solution and sample preparations.

Transient absorption measurements at four-second timescale

The same instrumental setup and sample preparations as described in the previous section were used. Instead of the Xe900 xenon lamp, a tungsten halogen lamp (50 W, 12 V) was employed as the probe beam because it was more stable over longer timescales.

4.4.3 Chemical Oxidation of **1** Using Independently Generated $\text{Ru}(\text{bpy})_3^{3+}$

$\text{Ru}(\text{bpy})_3^{3+}$ was independently generated using sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) for stoichiometric oxidation reactions of the Na salt of **1**. $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ has not been used as the sacrificial electron acceptor because both Co^{II} and Co^{III} are colored and will interfere with the signals from $\text{Ru}(\text{bpy})_3^{2+}$, **1**, and the product(s) formed. In addition, after $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ was reduced, a precipitate that was likely to be the poorly soluble $\text{Co}(\text{OH})_2$ formed, which would further complicate UV-visible spectroscopic measurements.

Each experiment was carried out in a dark room. Stock solutions of **1** and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ were prepared in the same way as those described above in the section “Transient Absorption Spectroscopic Measurements”. $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (2.5 mL of a 1.0 mM stock solution) was added to a Schlenk flask connected to a N_2 inlet, following which H_2O (2.5 mL) was added. $\text{Na}_2\text{S}_2\text{O}_8$ (6.0 mg) was then added to the solution, giving a composition of $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 0.50$ mM and $[\text{Na}_2\text{S}_2\text{O}_8] = 5.0$ mM. The solution was bubbled with N_2 for 10 minutes and then irradiated with blue LEDs (450 nm, ~ 1 W) for 10 minutes. The solution turned from orange-red ($\text{Ru}(\text{bpy})_3^{2+}$) to green ($\text{Ru}(\text{bpy})_3^{3+}$). For every experiment, an aliquot (0.20 mL, 1 equivalent or 0.40 mL, 2 equivalents) of the solution was drawn using a micropipette and added to a 1 mL volumetric flask. The Na salt of **1** (0.10 mL) in a 1.0 mM stock solution was measured using a micropipette and added into the $\text{Ru}(\text{bpy})_3^{3+}$ solution. The solution was diluted with appropriate volumes of ACN and H_2O to make up a total volume of 1 mL with a ratio of $\text{H}_2\text{O}:\text{ACN} = 1:1$, giving the final concentrations as $[\text{Ru}(\text{bpy})_3^{3+}] = 0.10$ mM (1 equivalent) or 0.20 mM (2 equivalents), and $[\mathbf{1}] = 0.10$ mM. The cuvette was then placed in a UV-visible spectrophotometer and its spectrum was recorded at regular time intervals.

4.4.4 Three-Electron Chemical Oxidation of **2**

The synthesis of tris(2,4-dibromophenyl)aminium ($[\text{Ar}(\text{Br})_2]_3\text{N}^{\bullet+}$) hexafluoroantimonate is depicted in Figure 4.15.

Figure 4.15 Synthetic route of $[\text{Ar}(\text{Br})_2]_3\text{N}^{\bullet+}\text{SbF}_6^-$.

Synthesis of tris(2,4-dibromophenyl)amine ([Ar(Br)₂]₃N)

The synthesis was modified from that described by Yueh and Bauld.⁷ Triphenylamine (1.2 g, 5.0 mmol) was dissolved in CHCl₃ (10 mL) in a 25 mL 2-neck round bottom flask, with one neck connected to a 10 mL addition funnel and another neck connected to an outlet. Bromine (Br₂, 1.5 mL, 60 mmol) was dissolved in CHCl₃ (5 mL) and transferred into the addition funnel. Br₂ solution was added dropwise over 5 minutes into the triphenylamine solution under vigorous stirring. Effervescence, accompanied with the liberation of white fumes, was observed during the addition of the first 2.5 mL of Br₂ solution. The dark brown Br₂ solution turned to pale yellow immediately upon mixing with the triphenylamine solution. The subsequent addition of 2.5 mL of Br₂ solution resulted in a dark brown solution with no effervescence observed. The solution was stirred for 12 hours, giving a brown-red solution. EtOH (75 mL) was then added into the reaction mixture, resulting in the formation of a white precipitate. The suspension was filtered and the residue was recrystallized in 2:1 CHCl₃:EtOH (5 mL) to give colorless crystalline material (3.3 g, 91%). ¹H NMR (CDCl₃, 500 MHz, Figure A.11): δ = 6.68 (d, J = 8.5 Hz, 6 H, ArH), 7.34 (dd, J = 8.5, 2.0 Hz, 6 H, ArH), 7.74 (d, J = 2.0 Hz, 6 H, ArH). The data is in agreement with that reported previously.⁷

Synthesis of tris(2,4-dibromophenyl)aminium radical-cation**hexafluoroantimonate ([Ar(Br)₂]₃N^{•+}SbF₆⁻)**

The synthesis was modified from that described by Murata *et al.*⁸ Compound [Ar(Br)₂]₃N (4.4 g, 6.1 mmol) was transferred into a 500 mL two-neck round bottom flask and was dissolved in anhydrous DCM (35 mL). The solution was cooled to 0 °C. Antimony pentafluoride (SbF₅, 0.65 mL, 9.0 mmol) was withdrawn using a 10 mL glass graduated pipette

prefilled with argon, and was added dropwise into the $[\text{Ar}(\text{Br})_2]_3\text{N}$ solution under a positive argon flow. The solution turned dark green immediately. After the addition was complete, the reaction mixture was allowed to warm to room temperature. Subsequently, anhydrous pentane (170 mL) was added into the reaction mixture, giving a dark green suspension. The product was then collected by Schlenk filtration. The dark green residue was washed with anhydrous carbon disulfide (CS_2 , 2 x 25 mL) and the resulting pale red CS_2 supernatant was drained. The dark green residue was dried *in vacuo* for 4 hours. The dried solid (2.1 g, 36%) was transferred into a glovebox and stored at $-30\text{ }^\circ\text{C}$.

Oxidation of **2 Using $[\text{Ar}(\text{Br})_2]_3\text{N}^{\bullet+}$**

Butyronitrile (PrCN) solvent was purified using procedures described by Van Duyne and Reilley.⁹ Stock solutions of **2** (0.10 mM) and $[\text{Ar}(\text{Br})_2]_3\text{N}^{\bullet+}\text{SbF}_6^-$ (50 mM) in PrCN were prepared in a glovebox. A solution of **2** (2.5 mL) was transferred into a 1 cm-path length cuvette, whereas the $[\text{Ar}(\text{Br})_2]_3\text{N}^{\bullet+}\text{SbF}_6^-$ solution was drawn into a microsyringe. The cuvette and microsyringe were taken out of the glovebox. The cuvette was cooled to $-80\text{ }^\circ\text{C}$. The $[\text{Ar}(\text{Br})_2]_3\text{N}^{\bullet+}\text{SbF}_6^-$ solution was added in successive 5 μL portions to the cooled solution of **2** under vigorous stirring and the corresponding UV-visible spectra were recorded. The reference spectrum of each experiment at the different temperatures was collected by using the same solvent cooled to the corresponding temperature.

Spectroelectrochemistry

The spectroelectrochemical cell was assembled by fitting a customized three-electrode setup (Latech Scientific Supply Pte. Ltd.) into a 1 mm-path length customized cuvette (Starna Scientific Ltd.). The

spectroelectrochemical cell was connected to a Bio-Logic SP-300 potentiostat. All samples in low temperature UV-visible spectroscopy experiments were cooled using a Unisoku USP-203-A cryostat connected to a Shimadzu UV-3600 or an Agilent Cary 8454 spectrophotometer.

Kinetics Studies on the Reaction of Three-Electron Oxidised **2 (**2**³⁺) with Thioanisoles**

Oxidized intermediate **2**³⁺ was generated using the procedures described in the section “Oxidation of **2** Using [Ar(Br)₂]₃N^{•+}”. The addition of [Ar(Br)₂]₃N^{•+}SbF₆⁻ was performed at 5 μL portions until a maximum absorbance at 585 nm was recorded. Then, using a microsyringe, an aliquot of *p*-substituted thioanisole (*p*-XC₆H₄SMe, X = NO₂, Me, OMe, 10 – 40 equivalents) solution in PrCN was injected into the solution of **2**³⁺ and the UV-visible spectrum of the reaction mixture was recorded using an Agilent Cary 8454 spectrophotometer at 0.5 – 2 second intervals. With reference to the absorbance at 585 nm, each kinetics data set was fitted to a mono-exponential function and the time constant was determined by a least-squares fitting procedure in Origin. The corresponding pseudo first-order constant, *k*_{obs}, was derived from the reciprocal of the time constant. The second-order rate constant, *k*, for the oxidation of *p*-XC₆H₄SMe by **2**³⁺ was determined from the linear fit of the plot of *k*_{obs} against the concentration of *p*-XC₆H₄SMe.

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Chapter 5

Anion-Dependent Valence Tautomerization

*Having determined that the photochemical oxidation of **1** is feasible in the previous chapter, this chapter begins with our efforts to degrade dyes photocatalytically using **1** as the catalyst, and $\text{Ru}(\text{bpy})_3^{2+}$ as the photosensitizer. Interestingly, we observed a counterintuitive, inhibitory effect in the photodegradation of dyes. Further investigation into the system revealed that oxidized **1** by an outer-sphere oxidant displays valence tautomerization, depending on the exogenous anions. Mechanistic studies have revealed that the reaction pathway contrasts with the conventionally accepted electrophilic halide reactivity of high valent Fe systems.*

The presence of labile Cl^- or Br^- results in a ligand-based oxidation and stabilization of a radical-cationic $(\text{TAML}\bullet^+)\text{Fe}^{\text{III}}$ complex, which subsequently leads to C-H activation and nucleophilic substitution on the TAML aryl ring. In contrast, exogenous cyanide culminates in metal-based oxidation, yielding the first $S = 1$ $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{CN})_2]^{2-}$. This is the only high valent, Fe^{IV} dicyanide complex characterized by X-ray crystallography.

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5.1 Introduction

From the electrochemical and photophysical characterizations of **1** (chapter 4), we have ascertained that **1** can be oxidized photochemically by the $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_3\text{Cl}_3$ photosensitizer system, giving a long-lived oxidized **1**. Therefore, we set out to use the photochemically oxidized **1** to perform degradation reactions that high valent (TAML) $\text{Fe}^{\text{V}}(\text{O})$ complexes are known for.¹ We wanted to explore the utilization of photoactivated **1** in various reactions (Figure 5.1).

Figure 5.1 Reaction scheme of the desired photoactivation of **1** for dye degradation.

Intriguingly, the (photo)chemically oxidized **1** undergoes anion-dependent valence tautomerization, giving (TAML) Fe^{IV} (**1⁺**) and (TAML $\bullet^+$) Fe^{III} (**1-TAML $\bullet^+$**), instead of the usual electrophilic halide reactivity among high-valent Fe complexes. Contrary to the enhanced activity in cytochrome P450 Compound I for hydrogen abstraction, however, our resulting ligand radical-cation (**1-TAML $\bullet^+$**) becomes susceptible to nucleophilic attack, which has never been reported for any (TAML)Fe complexes. Through spectroscopic and analytical studies of chemically-oxidized **1**, including

Mössbauer spectroscopy and mass spectrometry, we have observed high valent Fe species, and isolated and structurally characterized a (TAML)Fe^{IV} dicyanide product during our mechanistic studies. Our experiments indicate that sterically protected (TAML)Fe^{III} precursors will serve as more robust reagents in prospective photodriven oxidative transformations.

5.2 Results and Discussion

The zero-field Mössbauer spectrum of ^{57}Fe -labelled **1** ($^{57}\textbf{1}$) in 1:1 $\text{H}_2\text{O}:\text{ACN}$ consists of a major doublet (63%, isomer shift $\delta = 0.182 \text{ mm s}^{-1}$, quadrupole splitting $\Delta E_Q = 3.071 \text{ mm s}^{-1}$) and a minor doublet (34%, $\delta = 0.184 \text{ mm s}^{-1}$, $\Delta E_Q = 3.850 \text{ mm s}^{-1}$, Figure 5.2a). This mixed solvent combination was chosen to accommodate the disparate solubilities of **1** (soluble in ACN) and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, soluble in water). Both species are consistent with intermediate spin $S = 3/2$ ground states. To deduce the identities of these two species, Mössbauer spectroscopy was performed on $^{57}\textbf{1}$ dissolved in acetonitrile (Table 5.1 entry 2 and Figure 5.2b), and **1** as a solid (Table 5.1 entry 3 and Figure 5.2c). In all cases both species are present, indicating that they are not likely to be **1** coordinated to different axial solvent molecules.

We verified that the axial ligand(s) contained water molecules with an isotope-labelling experiment. Infrared (IR) spectroscopic measurement of **1**, after dissolution and heating at 50°C in D_2O for 15 minutes and then drying *in vacuo*, reveals new IR bands at 2382 and 2445 cm^{-1} (Figure 5.2d). These bands are slightly redshifted from those of D_2O (Figure 5.2e). When D_2O coordinates to the Fe metal center, the molecular orbital (MO) of D_2O would lose electron density. If the participating MO of D_2O happens to be non-bonding, then the O-D bond strength would not be affected, and thus a red-shift in the IR spectrum would not occur. Conversely, if the participating MO of D_2O is a bonding orbital, then the O-D bond strength would be weakened and consequently a red-shift in the IR spectrum would occur. Since a red-shift was observed experimentally, it suggests that the participating MO of D_2O contains bonding orbital(s). Computational studies can be used to calculate the decrease in the O-D bond strength when D_2O coordinates to the Fe metal center, and then correlate the decrease in

the bond strength to the decrease in the corresponding IR stretching frequency.

To predict the red-shift going from Fe(H₂O) to Fe(D₂O), we can treat the O-H and O-D bonds as springs, enabling the use of the following equation for a harmonic oscillator:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where ν is the IR stretching frequency (in wavenumber), k is the spring constant of the bond, c is the speed of light, and μ is the reduced mass of the A-B bond, which can be derived using the following equation:

$$\mu = \sqrt{\frac{m_A m_B}{m_A + m_B}}$$

where m_i is the mass of atom i .

Since

$$\nu \propto \sqrt{\frac{m_A + m_B}{m_A m_B}}$$

Hence

$$\begin{aligned} \frac{\nu_{O-H}}{\nu_{O-D}} &= \sqrt{\frac{\frac{m_O + m_H}{m_O m_H}}{\frac{m_O + m_D}{m_O m_D}}} \\ \frac{\nu_{O-H}}{\nu_{O-D}} &= \sqrt{\frac{\frac{16 + 1}{16(1)}}{\frac{16 + 2}{16(2)}}} \\ \nu_{O-D} &= \sqrt{\frac{9}{17}} (\nu_{O-H}) = \sqrt{\frac{9}{17}} (3300) = 2400 \text{ cm}^{-1} \end{aligned}$$

The estimated O-D stretch from the above calculation fits the experimentally observed new IR bands (2382 and 2445 cm^{-1} , Figure 5.2d). Therefore, we attribute these new IR bands to the exchange of H by D in the axially bound water molecule(s). Tentatively, we propose that the two Mössbauer signals arise from the 5- and 6-coordinate (TAML)Fe (**1** with one and two coordinated H_2O molecules at the axial position). Poor electron paramagnetic resonance (EPR) signal to noise ratios were observed for the Fe^{III} in **571** alone, possibly due to aggregation, as observed by Sullivan *et al.*⁴ Thus, no EPR spectroscopic data are presented here.

Figure 5.2 Mössbauer spectra of (a) 2 mM solution of **571** in 1:1 H_2O :ACN, (b) 2 mM solution of **571** in ACN, and (c) solid **1**. The black lines are the spectral simulations representing >95% of the absorption. The shaded areas are the spectral contributions from $^{57}\text{Fe}^{\text{III}}$ (black). A high-spin Fe^{III} impurity (5-10%) that we attribute to a deligated by-product, is observed in all cases. (d) Infrared spectra of **1** (black) and **1** after exchange with D_2O (red). Regions containing infrared bands of interest are marked with *. (e) Region containing O-D stretch (* in Figure 5.3d), with infrared signals from D_2O (blue). (f) Region containing O-H stretch (* in Figure 5.3d).

We subsequently investigated the photodegradation of methylene blue (MB) dye because its absorption band ($\lambda_{\text{max}} = 665 \text{ nm}$) is distinct from that of $\text{Ru}(\text{bpy})_3^{2+}$ ($\lambda_{\text{max}} = 450 \text{ nm}$). The results were unexpected. Complex **1** appeared to inhibit the degradation of MB (Figure 5.3) and other dye substrates like rhodamine B and methyl violet 2B.

Figure 5.3 Photodegradation of MB with the following reagent concentrations: $[\text{Co}(\text{NH}_3)_5\text{Cl}_3] = 10 \text{ mM}$, $[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 0.020 \text{ mM}$, $[\mathbf{1}] = 0.60 \text{ mM}$, and $[\text{MB}] = 0.60 \text{ mM}$. (a) UV-vis absorption spectra of the photodegradation of MB without **1** (control). (b) UV-vis absorption spectra of the photodegradation of MB with **1**. (c) Comparison between MB photodegradation in the presence of **1** and the control without **1**.

Negative-ion mode ESI-MS of the reaction mixture of $\text{Ru}(\text{bpy})_3^{3+}$ and **1** revealed high resolution ion peaks at mass-to-charge ratios of $m/z = 451.9977$ and 485.9579 (34 and 68 mass units higher than **1**), which could have arisen from the nucleophilic aromatic substitution of Cl (from $\text{Ru}(\text{bpy})_3\text{Cl}_2$) into the TAML ligand of **1**. We tentatively propose that the photochemical oxidation of **1** is predominantly ligand-based, leading to stabilization of a radical-cationic $(\text{TAML}\cdot^+)\text{Fe}^{\text{III}}$ (**1-TAML** $\cdot^+$), similar to Ce^{IV} oxidation in other TAML Fe systems.⁵ The oxidation of the TAML ligand results in the formation of a radical-cation (akin to Compound I in P450) that increases its susceptibility to nucleophilic attack, leading to aromatic substitution in the ligand by Cl^- . We propose that our observations arose from the use of an outer-sphere oxidant, $\text{Ru}(\text{bpy})_3^{3+}$, as compared to

the more commonly reported inner-sphere oxidants such as (organic) peroxides.

To evaluate this hypothesis, we chemically oxidized **1** in the presence of several anions to independently characterize the products. $(\text{ArMe})_3\text{N}^{\bullet+}$ (ArMe = 4-methylphenyl) has been chosen because it is an outer-sphere oxidant ($E^{0'}$ = 0.40 V vs Fc^+/Fc) suitable for only one electron oxidation of **1**.⁶ In addition, unlike the ^1H NMR spectroscopic signals of 2,2'-bipyridyl from $\text{Ru}(\text{bpy})_3^{2+}$, those of $(\text{ArMe})_3\text{N}$ do not overlap with the signals of the TAML ligand, therefore enabling the substituted TAML to be monitored by ^1H NMR spectroscopy after demetallation. Among the common anions inert towards $(\text{ArMe})_3\text{N}^{\bullet+}$, we screened Cl^- , Br^- , and CN^- anions.

Negative-ion mode ESI-MS data of the oxidized **1** in the presence of Br^- show masses and isotopic distributions corresponding to those of **1-TAML-(Br)** and **1-TAML-(Br)₂** (Figure 5.4a), where one and two bromides have substituted for hydrogens on the aromatic ring in **1**, respectively. X-ray photoelectron spectroscopy (XPS) measurements also substantiate the presence of aryl bromides (Figure 5.4b).⁷ To monitor the progress of the substitution reactions, aliquots were withdrawn at specific time intervals, quenched with $\text{Na}_2\text{S}_2\text{O}_3$ solutions, demetallated in pH 7 phosphate buffer solutions, and then analyzed by ^1H NMR spectroscopy. Within 15 minutes, the signals corresponding to TAML disappeared (grey dashed line), accompanied with the emergence of a set of new signals (orange dashed lines), which we propose to be mostly **1-TAML-(Br)₂** (Figure 5.4c). We assigned the major ^1H NMR signals (labelled as H_A , H_B , and H_C) to those of one **1-TAML-(Br)₂** isomer, while the remaining signals belong to the minor isomers of **1-TAML-(Br)₂** with Br substituted at other positions of the aryl ring (Figure 5.4c). We managed to isolate **1-TAML-(Br)₂** by reverse-phase C18 column chromatography, but we were not successful at

growing single crystals of this complex. TAML-(Br)₂ was derived from the demetallation of the isolated complex and was characterized by ¹H NMR spectroscopy (Figure 5.5).

Figure 5.4 Characterization data of **1-TAML-(Br)_n** generated from the reaction containing **1**, (ArMe)₃N^{•+} (4 eq), and tetraethylammonium bromide (TEABr, 10 eq). (a) Negative-ion ESI-MS of the crude reaction mixture 30 minutes after addition of the (ArMe)₃N^{•+} oxidant. The assigned intermediates are labelled. (b) Br 3d XPS data of **1-TAML-(Br)_n**. The fit (red, binding energy = 70.7 eV) represents the component completely attributable to aryl bromide. (c) ¹H NMR spectra of demetallated aliquots of the reaction mixture, withdrawn at time intervals 1 (red), 3 (blue), and 15 (green) minutes after addition of the (ArMe)₃N^{•+} oxidant. The spectrum of TAML before oxidation is shown in black. The dashed lines highlight the characteristic ¹H NMR signals from TAML (grey) and the proposed TAML-(Br)₂ (orange). The ¹H NMR signals (labelled as H_A, H_B, and H_C) are proposed to arise from the major TAML-(Br)₂ isomeric product, while the remaining signals (*) likely originate from another isomer of TAML-(Br)₂ with Br substitution at a different position of the aryl ring.

Figure 5.5 The ^1H NMR spectrum of the demetallated TAML-(Br) $_2$ ligand derived from acid hydrolysis of **1-TAML-(Br) $_2$** . The NMR signals assigned to the symmetrical TAML-(Br) $_2$ are marked with a red asterisk (*). The unassigned signals are proposed to be the asymmetrically bromide-substituted TAML-(Br) $_2$ or decomposed TAML-(Br) $_2$ during hydrolysis.

On the other hand, aromatic substitution of Cl^- proceeded more sluggishly, as evident from the longer reaction time and the moderate conversions of **1-TAML** to **1-TAML-(Cl)** and **1-TAML-(Cl) $_2$** , based on the ESI-MS data. As a result, the NMR signals resemble TAML and the minor products cannot be unambiguously assigned (Figure 5.6).

Figure 5.6 (a) Negative-ion ESI-MS of the crude reaction mixture containing **1** (1 eq), (ArMe)₃N^{•+} (4 eq), and TEACl (10 eq) 18 hours after addition of the (ArMe)₃N^{•+} oxidant. The assigned intermediates are shown. (b) Cl 2p XPS data. The fit (red) contains higher energy components (blue and green) assignable to aryl chloride, and lower energy components (grey and orange), corresponding to inorganic chloride ions. (c) ¹H NMR spectra of the demetallated aliquots of reaction mixture **1** (1 eq) + (ArMe)₃N^{•+} (4 eq) + TEACl (10 eq), withdrawn at time intervals 1 (red), 30 (blue), and 90 (green) minutes after addition of the (ArMe)₃N^{•+} oxidant. The spectrum of TAML before oxidation is shown in black. The dashed lines highlight the characteristic ¹H NMR signals from TAML (grey). Due to the moderate conversions of TAML to TAML-(Cl) and TAML-(Cl)₂, based on the ESI-MS data, the ¹H NMR signals at different time points suggest slow reaction of the TAML, with small amounts of isomeric mixtures of TAML-(Cl) and TAML-(Cl)₂ as minor products.

Having ascertained that substitution of Cl⁻ or Br⁻ into the TAML ligand had occurred upon oxidation of **1**, we proceeded to investigate the mechanism. To probe if there is any interaction between **1** and X⁻ (X = Cl or Br), the UV-visible spectra of a solution of **1** (0.2 mM in ACN) before (black, Figure 5.7a) and after the addition 10 equivalents of Cl⁻ (blue, Figure 5.7a) or 10 equivalents of Br⁻ (red,

Figure 5.7a) were recorded. No further changes were noted upon further UV-visible spectroscopic measurements. We propose that these changes arise from the exchange of the solvent molecule at the axial position with a halide, thus forming **1-X**, and this exchange reaches equilibrium quickly (within 3 minutes). In contrast, when CN^- was employed in place of halide anions, the UV-visible spectra of the mixture of **1** and 10 equivalents of CN^- reveal a more gradual equilibrium being achieved over 30 minutes (Figure 5.7b). Compared to the spectra of **1-X** ($\text{X} = \text{halide}$), a more distinct change in λ_{max} from 415 nm (from red, Figure 5.7b) to 440 nm (green, Figure 5.7b) is observed. In addition, the ESI-MS data show the presence of a mass fragment corresponding to $\text{K}[\text{1}^+-(\text{CN})_2]$ upon the oxidation of **1** in the presence of excess CN^- (Figure 5.13c). These results suggest that, in the presence of excess CN^- , two CN^- ligands can exchange with the axial solvent molecules of **1** to form **1-(CN)₂**.

Figure 5.7 (a) UV-vis spectrum of **1** (0.20 mM, black). UV-vis spectra of reaction mixtures of Br^- (10 eq) + **1** (red), and Cl^- (10 eq) + **1** (blue). The spectra of **1** in the presence of excess halide were measured at intervals of 3 minutes, and no further spectral changes were observed beyond 3 minutes. (b) UV-vis spectrum of **1** (0.20 mM, black) and the UV-vis spectral changes over time after the addition of CN^- (10 eq).

Subsequently, the oxidation of **1-X** should give **1⁺-X** (left, Figure 5.8). Apart from our proposed nucleophilic aromatic substitution on **1(X)-TAML^{•+}** (top, Figure 5.8), we also considered the possibility that the

coordinated halide on 1^+-X may be electrophilic. Intermolecular (middle, Figure 5.8) or intramolecular (bottom, Figure 5.8) electrophilic aromatic substitution could then result in the observed **1-TAML-(X)** products.

Figure 5.8 Possible mechanisms that could lead to the observed **1-TAML-(X)** products following the oxidation of **1-X**. The compounds marked in red arise from a second molecule of X^- or **1**, instead of the original **1-X** and its oxidized intermediates.

To probe if an intermolecular mechanism is involved, 1,4-dimethoxybenzene (DMOB) has been chosen as an electron-rich aromatic substrate, with straightforward ^1H NMR signals (singlets), to facilitate monitoring of the substitution reaction progress. The ^1H NMR spectra before (top, Figure 5.9a) and after oxidation (middle and bottom, Figure 5.9a) show mainly unreacted DMOB (blue dashed lines) and no new NMR signals that can be attributed to the brominated DMOB. Gas chromatography-mass spectrometry (GC-MS) measurements on the oxidized reaction mixture confirmed the absence of brominated DMOB as well. Similar to previous experiments in the absence of DMOB, the ESI-MS data of the oxidized reaction mixture shows **1-TAML-(Br)_n** (Figure 5.9b-c), indicating that the bromide substitution reaction occurs exclusively

at the TAML ligand despite the presence of the electron-rich DMOB. These results suggest that an *intermolecular* electrophilic aromatic substitution mechanism is not operational.

Figure 5.9 (a) ^1H NMR spectra of reaction mixture containing DMOB (1 eq), **1** (1 eq), and TEABr (10 eq), before (top), 5 minutes after (middle), and 24 hours after (bottom) the addition of (ArMe) $_3\text{N}^{\bullet+}$ (2 eq). The characteristic ^1H NMR signals from DMOB (blue dashed lines) and (ArMe) $_3\text{N}^{\bullet+}$ (■) are labelled. The ^1H NMR signals marked by * originate from TAML-(Br) $_n$ (Figure 5.6), formed from the demetallation of **1**(Br)-TAML-(Br) $_n$. Negative-ion ESI-MS of the reaction mixture of **1** (1 eq) + DMOB (1 eq) + Br $^-$ (10 eq), before (b) and 5 minutes after (c) the addition of (ArMe) $_3\text{N}^{\bullet+}$ oxidant (2 eq). The assigned intermediates are labelled. The signals marked with * are assigned to TAML-(Br) (red), TAML-(Br) $_2$ (blue), and [TAML-(Br) $_3$ (orange).

To explore the feasibility of an *intramolecular* electrophilic aromatic substitution mechanism, we conducted kinetics measurements to evaluate the rate dependence on the concentration of exogenous bromide. We prepared a solution of **1-Br** (generated in situ by mixing **1** with >10 equivalents of Br $^-$ for 5 minutes) and reacted it with 2 equivalents of

(ArMe)₃N^{•+}, with varying concentrations of Br⁻. By monitoring the decay of the UV-visible spectral signals of the oxidized **1-Br** over time at the absorption maximum of 893 nm (Figure 5.10a), we fit the kinetics data (inset of Figure 5.10a) to obtain the corresponding pseudo first-order rate constant, k_{obs} . If the reaction occurs due to nucleophilic attack of Br⁻ on the **1(Br)-TAML^{•+}** radical cation as we proposed, the k_{obs} should increase with increasing Br⁻ concentration. Conversely, the k_{obs} from an intramolecular electrophilic aromatic substitution should be independent of the Br⁻ concentration. The plot of k_{obs} against Br⁻ concentration reveals a positive linear correlation, giving a second-order rate constant k of $1.2 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for the aromatic substitution of oxidized **1-Br** (Figure 5.10b). In a separate experiment, analysis of ESI-MS data from the reaction of 10 equivalents of Br⁻ with oxidized **1-Cl** (generated in situ by adding 2 equivalents of (ArMe)₃N^{•+} to a solution of 1 equivalent of Cl⁻ and **1**) reveals predominantly **1-TAML-(Br)_n** products being formed instead of the **1-TAML-(Cl)_n** products expected for an intramolecular chloride migration (Figure 5.10c-d). Patently, the subsequently added Br⁻ has substituted on the aromatic ring in **1** ahead of the already coordinated Cl⁻. These results indicate that the conventional electrophilic halide aromatic substitution pathways are not operating for our system, and instead support our proposed atypical mechanism, where **1(X)-TAML^{•+}** is attacked by an external anion to form the **1-TAML-(X)** products.

Figure 5.10 (a) UV-visible spectral changes from the reaction between oxidized **1-Br** (0.20 mM) and TEABr (2.0 mM) in ACN. The inset shows the absorbance decay monitored at 893 nm (a characteristic band of the oxidized **1-Br**), and the solid red line shows the fit to the kinetics. (b) Plot of k_{obs} against Br^- concentration. The linear fit of the data gives a second-order rate constant, k , for the aromatic substitution of oxidized **1-Br**. Negative-ion ESI-MS of the reaction mixture of **1** (1 eq) + Cl^- (1 eq) + $(\text{ArMe})_3\text{N}^{\bullet+}$ oxidant (2 eq) before (c) and after (d) the addition of Br^- (10 eq). The signal marked with a red * is assigned to the demetallated TAML-(Br).

Mössbauer spectroscopic analysis on ^{57}Fe -enriched **1** ($^{57}\textbf{1}$) was carried out to obtain further insights into the oxidation process. Without strong nucleophiles present (exogenous anions), the oxidation of $^{57}\textbf{1}$ gives a new species ($\delta = 0.153 \text{ mm s}^{-1}$, $\Delta E_Q = 3.843 \text{ mm s}^{-1}$, Figure 5.11a; blue component), typical of $S = 3/2$ (TAML) Fe^{III} complexes (Table 5.1 entry 4). This clearly supports ligand-based oxidation of $^{57}\textbf{1}$, forming $^{57}\textbf{1-TAML}\bullet^+$. In the presence of labile Br^- , the Mössbauer spectrum of the oxidized product (1 min after oxidation) shows a mixture of species comprising of 63% of $^{57}\textbf{1(Br)-TAML}\bullet^+$ and 29 % of a new species ($\delta = -0.161 \text{ mm s}^{-1}$, $\Delta E_Q = 3.232 \text{ mm s}^{-1}$; Table 5.1 entry 7), which we assign to the formation of $S = 1$ (TAML) $^{57}\text{Fe}^{\text{IV}}(\text{Br})$ ($^{57}\textbf{1}^+-\text{Br}$, red component in Figure 5.11b). The major $^{57}\textbf{1(Br)-TAML}\bullet^+$ component undergoes nucleophilic attack by Br^- to eventually form $^{57}\textbf{1-TAML-(Br)}_2$ ($\delta = 0.125 \text{ mm s}^{-1}$, $\Delta E_Q = 4.000 \text{ mm s}^{-1}$; Table 5.1 entry 8) as the sole product in 90 mins (bottom, Figure 5.12). Similar valence tautomerization is observed between $^{57}\textbf{1(Cl)-TAML}\bullet^+$ and $^{57}\textbf{1}^+-\text{Cl}$ in the presence of Cl^- (Figure 5.11c), but the equilibrium markedly shifts to the $\text{Fe}^{\text{IV}} ^{57}\textbf{1}^+$ form (Table 5.1 entry 5).

Figure 5.11 Mössbauer spectra of (a) $^{57}\mathbf{1}$ and $\text{Ru}(\text{bpy})_3^{3+}$, (b) $^{57}\mathbf{1}$, $\text{Ru}(\text{bpy})_3^{3+}$, and Br^- , (c) $^{57}\mathbf{1}$, $\text{Ru}(\text{bpy})_3^{3+}$, and Cl^- , (d) $^{57}\mathbf{1}^+-(\text{CN})_2$. All $\text{Ru}(\text{bpy})_3^{3+}$ oxidant solutions were generated photochemically from $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ precursors to minimize interference from the exogenous anions. Samples (a) to (c) were taken 1 minute after the addition of the oxidant. The black lines are the simulations representing >95% of the absorption. Shaded areas are the spectral contributions from $^{57}\mathbf{1}\text{-TAML}\bullet^+$ (blue) and $^{57}\mathbf{1}^+$ (red). A high-spin Fe^{III} impurity (5-10%) that we attribute to a deligated by-product, is observed in all cases.

Table 5.1 Summary of the Mössbauer results.

Entry	Reaction Mixture	ΔE_Q (mm s ⁻¹)	δ (mm s ⁻¹)	Percentage ^a (%)	Assigned Fe species
1	⁵⁷1 ^b	3.071	0.182	63	Fe ^{III}
		3.850	0.184	34	
2	⁵⁷1 ^c	3.071	0.186	73	Fe ^{III}
		3.844	0.186	27	
3	1 ^d	3.949	0.195	88	Fe ^{III}
		3.158	0.208	12	
4	⁵⁷1 + Ru ^{III} (bpy) ₃ ³⁺ (1 eq) ^b	3.843	0.153	93	Fe ^{III} -TAML• ⁺
5	⁵⁷1 + Ru ^{III} (bpy) ₃ ³⁺ (4 eq) + Cl ⁻ (10 eq), 1 min ^b	3.123	-0.075	71	Fe ^{IV} -Cl
		3.542	0.105	29	Fe ^{III} (Cl)-TAML• ⁺
6	⁵⁷1 + Ru ^{III} (bpy) ₃ ³⁺ (4 eq) + Cl ⁻ (10 eq), 30 mins ^b	3.123	-0.103	56	Fe ^{IV} -Cl
		3.547	0.183	40	Fe ^{III} -TAML-(Cl) _n
7	⁵⁷1 + Ru ^{III} (bpy) ₃ ³⁺ (4 eq) + Br ⁻ (10 eq), 1 min ^b	3.580	0.152	63	Fe ^{III} (Br)-TAML• ⁺
		3.232	-0.161	29	Fe ^{IV} -Br
8	⁵⁷1 + Ru ^{III} (bpy) ₃ ³⁺ (4 eq) + Br ⁻ (10 eq), 90 mins ^b	4.000	0.125	85	Fe ^{III} -TAML-(Br) ₂
9	⁵⁷1 ⁺ -(CN) ₂ ^c	2.977	-0.141	80	Fe ^{IV} -(CN) ₂

^a There is a small contribution (the remainder of the sample) from ⁵⁷Fe species with an unusual ΔE_Q (0.3 – 0.7 mm s⁻¹) and δ (0.2 – 0.5 mm s⁻¹), which we believe to arise from deligated (TAML)Fe (unshaded region of the Mössbauer spectra). ^b Samples were dissolved in 1:1 H₂O:ACN. ^c Samples were dissolved in ACN. ^d Sample was measured as a solid.

Figure 5.12 Proposed mechanism for the oxidation of **1**, followed by valence tautomerization between **1(X)-TAML•⁺** and **Fe^{IV}** intermediates, depending on the exogenous anion.

Intriguingly, in the presence of excess (10 equivalents) CN^- , the UV-visible measurements of **1** reveal a slow formation of a new absorption band with $\lambda_{\text{max}} = 440 \text{ nm}$ (green, Figure 5.7b), which is not observed in the case of Cl^- or Br^- . We attribute this observation to the formation of **1-(CN)₂** (top center, Figure 5.12). Upon oxidation with $(\text{ArMe})_3\text{N}\bullet^+$, no signal of **1-TAML-(CN)_n** was observed by negative-ion mode ESI-MS despite prolonged stirring (24 hours). Furthermore, the black solution observed upon addition of $(\text{ArMe})_3\text{N}\bullet^+$ remained black, unlike the Br^- and Cl^- experiments, where red suspensions were observed. We hypothesized that CN^- might have a stabilizing effect on **1⁺**, instead of undergoing nucleophilic substitution with **1-TAML•⁺** to give **1-TAML-(CN)_n**.

We subsequently characterized the proposed CN^- -stabilized $\mathbf{1}^+$ species. UV-vis spectroscopic measurement of the crude reaction mixture showed three characteristic peaks at 600, 677, and 837 nm, with an estimated lifetime, $\tau_{837\text{nm}}$, of 4.4 ± 0.7 hours at room temperature (Figure 5.13a-b).

Having determined that the CN^- -stabilized $\mathbf{1}^+$ was not stable in solution at room temperature, we modified the procedures. Oxidation of $\mathbf{1}-(\text{CN})_2$ appeared to solely stabilize the one electron-oxidized $\mathbf{1}^+$ as $[(\text{TAML})\text{Fe}^{\text{IV}}(\text{CN})_2]^{2-}$ ($\mathbf{1}^+-(\text{CN})_2$, top right, Figure 5.12). Negative-ion mode cold-spray ionization-mass spectrometry (CSI-MS) conducted on the crude reaction mixture at -40°C revealed that majority of the Fe^{IV} complex was the mono-anionic $\mathbf{1}^+-\text{CN}$, while a small proportion was identified as the di-anionic complex paired with K^+ , $\text{K}[\mathbf{1}^+-(\text{CN})_2]$ (Figure 5.13c). Using IR spectroscopy (Figure 5.13d), we observed a blue-shift in the $\text{C}\equiv\text{N}$ stretch on going from KCN (2076 cm^{-1}) to $[\text{Fe}^{\text{III}}-\text{CN}]$ (2098 cm^{-1}) to $[\text{Fe}^{\text{IV}}-\text{CN}]$ (2127 cm^{-1}), consistent with CN^- being coordinated to an increasingly Lewis acidic Fe metal center, with the highest oxidation state Fe^{IV} being most electrophilic. Raman spectroscopic measurements did not give any observable signals for the $\text{C}\equiv\text{N}$ vibration.

We isolated the CN^- -stabilized Fe^{IV} complex $(\text{PPh}_4)_2[\mathbf{1}^+-(\text{CN})_2]$ and grew single crystals of the dark blue complex for X-ray crystallography (Figure 5.13e). The data was refined to give a disorder model with the TAML ligand occupying two positions, although there was no disorder in the $\text{Fe}-(\text{CN})_2$ core (Figure A.13 in Appendix). Other crystallographic parameters are in Tables A.8-12 in Appendix. Mössbauer measurements were performed to confirm the oxidation state of iron in $\mathbf{1}^+-(\text{CN})_2$. A major doublet ($\delta = -0.141\text{ mm s}^{-1}$, $\Delta E_Q = 2.977\text{ mm s}^{-1}$, Figure 5.11d; red component) is consistent with an $S = 1$ Fe^{IV} centre (Table 5.1, entry 9). To the best of our knowledge, this is the first crystal structure of a high valent cyano Fe^{IV} TAML complex, although Collins and coworkers had

spectroscopically characterized a square pyramidal $[\text{Fe}^{\text{IV}}(\text{DCB})(\text{CN})]^-$ mono-cyanide before.^{5b,8} Notably, our finding adds to a unique collection of high-valent cyano Fe^{IV} complexes,⁹ with ours being the first, di-anionic, octahedral $(\text{TAML})\text{Fe}^{\text{IV}}$ dicyanide complex to be characterized by X-ray crystallography. We also characterized the purified $\mathbf{1}^+-(\text{CN})_2$ using UV-visible spectroscopy (Figure 5.13f).

Careful scrutiny of the oxidized products of **1** in the presence of different anions (Cl^- , Br^- , CN^-), therefore, suggests valence tautomerization between $\mathbf{1}^+$ and $\mathbf{1-TAML}\bullet^+$ (Figure 5.12), governed by the exogenous anion. Since CN^- is a stronger σ donor and a stronger π acceptor compared to Cl^- and Br^- , CN^- binds more strongly to the Fe metal center. As a result, the d_z^2 orbital of the Fe metal center is raised. We propose that the d_z^2 orbital of the Fe metal center is very similar in energy to the ligand-based orbital. Hence, having an axial CN^- ligand will raise the d_z^2 orbital to become the HOMO, giving rise to a metal-based oxidation to give an Fe^{IV} complex. Conversely, the HOMOs of Cl^- - and Br^- -coordinated Fe complexes are ligand-based orbitals, resulting in ligand-based oxidation to yield an $\text{Fe}^{\text{III}}\text{-TAML}\bullet^+$ complex. This proposal can be verified using computational studies.

Figure 5.13 (a) UV-vis spectrum of **1** (orange) and the UV-vis spectral changes over time upon oxidation of **1** by $(\text{ArMe})_3\text{N}^+$ (1.05 eq) in the presence of excess of CN^- (5 eq.). (b) The change in absorbance, monitored at 837 nm over time. The mono-exponential fit is the line in red. Characterization data of the CN^- -stabilized 1^+ product generated from the reaction **1** + 5 eq. KCN + 1.05 eq. $(\text{ArMe})_3\text{N}^+$. (c) Negative-ion CSI-MS and the assigned intermediates in the crude reaction mixture containing the dianionic (TAML) Fe^{IV} complex $[1^+-(\text{CN})_2]^{2-}$. (d) Infrared spectra of KCN (black, $\nu_{\text{max}}/\text{cm}^{-1}$ 2076 (KCN)); **1** + 5 eq. KCN (red, $\nu_{\text{max}}/\text{cm}^{-1}$ 2098 ($\text{Fe}^{\text{III}}\text{-CN}$)); and **1** + 5 eq. KCN + 1.05 eq. $(\text{ArMe})_3\text{N}^+$ (blue, $\nu_{\text{max}}/\text{cm}^{-1}$ 2127 ($\text{Fe}^{\text{IV}}\text{-CN}$)). (e) X-ray crystal structure of the dianionic Fe^{IV} TAML complex $[(1^+-(\text{CN})_2)(\text{PPh}_4)_2]$. The hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at 50% probability. Selected bond lengths ($\text{\AA}$): Fe1-C20 2.011(6), Fe1-C21 1.993(6), C20-N5 1.137(7), C21-N6 1.141(7). (f) UV-visible spectrum of a 0.62 mM purified $1^+-(\text{CN})_2$ solution. $\lambda_{\text{max}}(\text{DCM})/\text{nm}$ 352 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1800), 452 (550), 596 (540), 639 (540), 728 (290), and 855 (160).

5.3 Conclusions

In summary, we have shown that **1** can be oxidized by photoexcited $\text{Ru}(\text{bpy})_3^{2+*}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$. Through mechanistic studies, kinetics measurements, MS, and Mössbauer spectroscopy, we show that ligand-based oxidation occurs to give **1-TAML•⁺** in equilibrium with Fe^{IV} , instead of the conventional electrophilic halide reactivity. The extent of valence tautomerization depends on the exogenous anions present. A strongly-coordinating CN^- will become an axial ligand to stabilize Fe^{IV} , and we have isolated and structurally characterized an unprecedented dicyano (TAML) Fe^{IV} complex. On the other hand, labile halides favor the Fe^{III} **1-TAML•⁺** tautomer, which is susceptible to nucleophilic substitution on the ligand. Similar nucleophilic reactions could arise in other Fe complexes, especially under harsh pollutant degradation, water oxidation, or C-H activation conditions, leading to catalyst modification.

From a broader perspective, our findings highlight some of the important aspects for developing photodriven biomimetic oxidation catalysts and an uncommon mechanism for high-valent iron reactivity. Currently, the most common oxidants to access high-valent iron species are inner-sphere reagents like peroxides or hypervalent iodine reagents. We report the generation of this unique **1-TAML•⁺** rather than the established (TAML) Fe^{IV} or Fe^{V} motifs, by using photochemically produced $\text{Ru}(\text{bpy})_3^{3+}$. Although valence tautomerization is observed in some synthetic porphyrinoid counterparts,¹⁰ anion-dependent valence tautomerization in non-heme iron systems are uncommon.⁵ Most significantly, the reported radical-cations often show enhanced substrate C-H activation behavior,¹¹ similar to reports on cytochrome P450, and recently on $\text{Mn}^{\text{IV}}(\text{O-LA})(\text{TBP8Cz}^{\bullet+})$ (LA = Lewis acid, TBP8Cz = octakis(p-tert-butylphenyl)corrolazinato³⁻) as well.^{10b} However, we show

that radical-cations on sterically unprotected ligands are susceptible to nucleophilic attack. Such unexpected reactivity of the high valent complexes with the exogenous compounds should be taken into consideration when designing new catalysts for oxidation reactions. These insights should be valuable in future studies and improvements to the designs of biomimetic high valent catalysts.

5.4 Materials and Methods

5.4.1 General Information

Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry (TCI). Unless otherwise stated, the commercial reagents were used as purchased. All reactions involving air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under a nitrogen atmosphere. All UV-visible absorption measurements were carried out on a Shimadzu UV-3600 spectrophotometer, except for kinetics measurements, where an Agilent Cary 8454 spectrophotometer was used instead. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were used as received. The ^1H and ^{13}C NMR spectroscopic measurements were recorded on a Bruker AV-500 (500 MHz) NMR spectrometer. The ^1H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield referenced to the residual protons of the deuterated solvents.

High-resolution mass spectra (HR-MS) were obtained with a Q-ToF Premier LC HR mass spectrometer. Cold-spray ionization-mass spectrometry (CSI-MS, negative ion mode) was performed using an AccuTOF (JEOL) mass spectrometer equipped with a CSI source. The following conditions were used: needle voltage = -2.0 kV; orifice 1 voltage = 0 V; ring lens voltage = -50 V; and spray temperature = -40 °C. X-ray photoelectron spectroscopy (XPS) data were acquired using a Phoibos 100 spectrometer and a Mg X-ray source (SPECS, Germany). XPS samples were prepared inside a glovebox with a nitrogen atmosphere and SPI double-sided adhesive carbon tape was used to hold the sample on the sample plate. The XPS data were calibrated based on the C 1s position at 284.6 eV and processed using the program CasaXPS. Elemental analyses

were performed with an Elementar vario MICRO cube analyzer. Infrared spectroscopic measurements were carried out on a Bruker VERTEX 80 spectrophotometer.

Mössbauer spectra in the absence of magnetic fields were each recorded on a SEECO MS6 spectrometer that consisted of the following instruments: a JANIS CCS-850 cryostat, including a CTI-CRYOGENICS closed-cycle 10 K refrigerator and a CTI-CRYOGENICS 8200 helium compressor. The cold head and sample mounts are equipped with calibrated DT-670-Cu-1.4L silicon diode temperature probes and heaters. The temperatures are controlled by a LAKESHORE 335 temperature controller. Spectra are recorded using a LND-45431 Kr gas proportional counter with a beryllium window connected to a SEECO W204 γ -ray spectrometer that includes a high voltage supply, a 10 bit and 5 μ s ADC, and two single channel analyzers. Motor control and recording of spectra is managed by a W304 resonant γ -ray spectrometer. For the reported spectra, a RIVERTEC MCO7.114 source (^{57}Co in Rh matrix) with an activity of about 1 GBq was used. The spectra were recorded at 17 K and the data were accumulated for about 1 week for each sample. Mössbauer data were processed and simulated using the WMOSS4 program (www.wmoss.org). Isomeric shifts are referenced to α -iron at room temperature.

5.4.2 Mössbauer Spectroscopy

^{57}Fe is a Mössbauer-active nucleus that absorbs γ -ray of certain energy level depending on the chemical environment of the ^{57}Fe sample. In Mössbauer spectroscopy, a ^{57}Fe sample is irradiated with a γ -ray beam of varying energy, and the transmitted beam is concurrently recorded. At the resonant energy level, i.e. when the ^{57}Fe sample absorbs the most γ -ray beam, a dip in the transmitted beam intensity is recorded. Hence, a plot of transmitted beam intensity against

incident γ -ray energy (as a function of velocity due to the use of Doppler effect to generate γ -ray of different energy) allows for important information such as the isomer shift (δ) and the quadruple splitting (ΔE_Q) to be derived. The δ gives information about the oxidation state of the ^{57}Fe sample, whereas the ΔE_Q provides insights into the spin state and the symmetry of the ^{57}Fe sample. In this project, we utilized the δ and the ΔE_Q obtained from Mössbauer spectroscopic measurement to determine the compositions of $\text{Fe}^{\text{III}}\text{-TAML}\bullet^+$ and Fe^{IV} in a sample.

The synthesis of $^{57}\text{FeCl}_2$ was adapted from *Inorganic Syntheses*.² Metallic ^{57}Fe (Isoflex USA, 95.78% enriched, 10 mg, 0.18 mmol) was added to a 10 mL Schlenk flask and was suspended in anhydrous MeOH (1 mL). Concentrated hydrochloric acid (~12 M, 40 μL , ~0.48 mmol) was added to the suspension. The mixture was bubbled with N_2 for 5 minutes. The Schlenk flask was sealed and heated at 100 $^\circ\text{C}$ for 3 hours. The resulting light green suspension was worked up by Schlenk filtration. The residue was washed with anhydrous MeOH (3 x 1 mL), filtered, and the combined organic phases were dried *in vacuo* to give an off-white solid. The solid was then dried further *in vacuo* at 100 $^\circ\text{C}$ for 4 hours to yield $^{57}\text{FeCl}_2$ as a beige powder. The PPh_4^+ salt of **571** was synthesized by employing the same procedure as that for the PPh_4^+ salt of **1**, but with $^{57}\text{FeCl}_2$ being the limiting reagent.

Each Mössbauer sample was prepared by adding appropriate equivalents of the reagent(s) to a 2 mM 1:1 ultrapure $\text{H}_2\text{O}:\text{ACN}$ solution of **571**. $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ (with PF_6^- as the counter anion) was generated photochemically in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ using the same procedure described in the section 4.4.3. LiCl and LiBr were used as the Cl^- and Br^- sources respectively, and were dissolved together with **571** before addition of the oxidant. Upon adding the reagent(s) to the **571** solution, the mixture was shaken vigorously. Subsequently, a ~0.5 mL aliquot was withdrawn

and added to a pre-cooled Mössbauer cup. The half-filled Mössbauer cup was frozen in liquid nitrogen and Mössbauer spectroscopic measurements were conducted on each sample.

Mössbauer spectroscopic measurements and most of the analysis of the data were performed by our collaborators, Ms. Xenia Engelmann and Dr. Kallol Ray (Humboldt Universität zu Berlin).

5.4.3 Photocatalytic Methylene Blue (MB) Degradation

An 8.0 mL $\text{H}_2\text{O}:\text{ACN} = 3:1$ solution containing $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ (10 mM), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.020 mM), **1** (0.60mM), and MB (0.60 mM), was prepared. Ar gas was bubbled through the solution for 10 minutes. The contents of the flask were irradiated with blue LEDs (450 nm, ~1 W). At specific time intervals, under positive Ar pressure, a 0.90 mL aliquot was withdrawn and centrifuged (Eppendorf Centrifuge 5424R, 13,000 rpm) for 45 minutes. The supernatant was carefully retrieved and was measured using UV-visible spectroscopy. The absorbance at 665 nm was used as an indicator of the concentration of MB. The experiments were repeated at least twice to obtain the mean and the standard deviation.

5.4.4 Synthesis of Tri(*p*-tolyl)amine ((ArMe)₃N) and Tri(*p*-tolyl)aminium Radical-Cation ((ArMe)₃N^{•+})

The synthesis was modified from that described by Goodbrand and Hu.³ The reaction scheme is shown in Figure 5.14.

Figure 5.14 Reaction scheme depicting the syntheses of (ArMe)₃N and (ArMe)₃N^{•+}, and the oxidation of **1** by (ArMe)₃N^{•+} in the presence of different nucleophiles. Nu⁻: nucleophile.

Synthesis of tri(*p*-tolyl)amine ((ArMe)₃N). Compound *p*-toluidine (2.14 g, 20.0 mmol), 4-iodotoluene (9.16 g, 42.0 mmol), potassium hydroxide (8.75 g, 150 mmol), anhydrous copper(I) chloride (77 mg, 0.78 mmol), and 1,10-phenanthroline (140 mg, 0.80 mmol) were suspended in anhydrous toluene (20 mL). Three freeze-pump-thaw cycles were applied to remove dissolved O₂ from the suspension. The mixture was then sealed and heated at 120 °C for 72 hours, and completion was confirmed by TLC. The reaction mixture was diluted with water (100 mL) and extracted with 3 x 150 mL hexane. The organic fractions were combined and rinsed with saturated NaHCO₃ solution (100 mL). The combined organic fractions were dried over anhydrous Na₂CO₃ and filtered. The hexane was removed by rotary evaporation to yield a dark brown precipitate. The precipitate was purified using flash column chromatography and eluted with hexane:DCM = 9:1. Upon solvent removal by rotary evaporation, colorless crystals of (ArMe)₃N (4.14 g, 72%) were obtained. ¹H NMR (DMSO-*d*₆, 500 MHz, Figure A.12 in Appendix): δ = 2.24 (s, 9 H, Me), 6.84 (d, *J* = 13.5 Hz, 6 H, ArH), 7.06 (d, *J* = 13.5 Hz, 6 H, ArH). The data concurs with that reported previously.³

Synthesis of tri(*p*-tolyl)aminium radical-cation ((ArMe)₃N^{•+}). This reaction was performed without Schlenk techniques. Compound (ArMe)₃N (75 mg, 0.26 mmol) and PbO₂ (155 mg, 0.65 mmol) were suspended in

ACN (3.0 mL). Hydrofluoroboric acid (HBF₄, min. 40%, 57 mL, 0.26 mmol) was added to the suspension, giving a dark blue suspension. The mixture was filtered and the dark blue filtrate containing (ArMe)₃N^{•+} was used in situ for subsequent reactions.

5.4.5 Oxidation of **1** in the Presence of Anions

Oxidation of **1 in the presence of bromide anions.** This reaction was performed without any Schlenk techniques. The Na salt of **1** (30 mg, 0.065 mmol), ^tBuOK (31 mg, 0.27 mmol), and tetraethylammonium bromide (TEABr, 140 mg, 0.65 mmol) were suspended in ACN (30 mL) and sonicated for about 30 seconds until the red solution turned into a green suspension. The (ArMe)₃N^{•+} (4 equivalents) generated in situ was added dropwise to the suspension, resulting in a black solution. Within 30 minutes, the black solution turned brown, and then red, accompanied by the formation of a white precipitate. Upon completion of the reaction, as monitored by negative-ion mode ESI-MS, the suspension was filtered and the red filtrate was diluted with diethyl ether (Et₂O, 50 mL), giving an orange precipitate. The precipitate was filtered and washed with Et₂O (10 mL) and water (5 mL). The residue was dissolved in MeOH (5 mL) and filtered. The solvent of the filtrate was removed by rotary evaporation to give the crude TEA[**1-TAML-(Br)**₂] product. C18 reverse-phase preparative column chromatography (Merck LiChroprep ®RP-18, 40 – 63 mm) was utilized to further purify the crude product. HR-MS (ESI-, *m/z*) calculated for C₁₉H₁₂⁷⁹Br⁸¹BrFeN₄O₄ (**1-TAML-(Br)**₂) [M - H]⁻ *m/z* = 575.8554, found 575.8566. The XPS (Br 3d) binding energy = 70.7 eV. Despite many attempts through different solvent combinations, different counter cations (PPh₄⁺ and PPN⁺), and different temperatures, single crystals of **1-TAML-(Br)**₂ could not be obtained. To gather further structural information of **1-TAML-(Br)**₂, purified **1-TAML-(Br)**₂ was

suspended in 1:9 MeOH: pH 5 acetate buffer solution to induce demetallation of **1-TAML-(Br)₂** to give TAML-(Br)₂, which was diamagnetic and therefore could be measured by ¹H NMR spectroscopy.

Oxidation of 1 in the presence of chloride anions. The same experimental procedures as those for Br⁻ were employed, with TEABr being replaced by tetraethylammonium chloride (TEACl). HR-MS (ESI-, *m/z*) calculated for C₁₉H₁₃ClFeN₄O₄ (**1-TAML-(Cl)**) [M - H]⁻ *m/z* = 451.9975, found 451.9977; and C₁₉H₁₂Cl₂FeN₄O₄ (**1-TAML-(Cl)₂**) [M - H]⁻ *m/z* = 485.9585, found 485.9579. XPS (Cl 2p) measurements revealed two sets of signals: one set has a 2p_{3/2} binding energy = 197.8 eV (grey) and a 2p_{1/2} binding energy = 199.3 eV (orange), matching that of inorganic Cl⁻, while the second set has a 2p_{3/2} binding energy = 200.4 eV (blue) and a 2p_{1/2} binding energy = 201.9 eV (green) (Figure 5.7b).

Oxidation of 1 in the presence of cyanide anions. This modified reaction was performed without any Schlenk techniques. The Na salt of **1** (30 mg, 0.065 mmol), ^tBuOK (8.0 mg, 0.072 mmol), and potassium cyanide (KCN, 21 mg, 0.32 mmol) were suspended in ACN (AR grade, 5 mL) and sonicated for about 30 seconds until the red solution turned into a green suspension. The suspension was cooled to 0 °C with stirring. (ArMe)₃N^{•+} (1.05 equivalents) generated in situ was added dropwise to the suspension, resulting in a black solution. After one minute of stirring, the solvent was removed on a Schlenk line at 0 °C. Once dried, the resulting black-grey solid (stable at room temperature under inert gases), was transferred into a glovebox for subsequent workup. In a glovebox, the solid was suspended in Et₂O (20 mL) and filtered. The black residue was washed with Et₂O (2 x 10 mL) and dichloromethane (DCM, 10 mL). The black residue was then dissolved in ACN (4 mL) and filtered. Tetraphenylphosphonium chloride (PPh₄Cl, 50 mg, 0.13 mmol) was added to the black filtrate, giving a dark

blue mixture. The solvent was then evaporated *in vacuo*. The dried residue was suspended in DCM (5 mL) and filtered to remove KCl. The dark blue filtrate was dried *in vacuo*. The residue was dissolved in ACN (0.5 mL), and recrystallized via vapor diffusion of Et₂O (5 mL) into the ACN solution at -30 °C. After five days, the supernatant was decanted to reveal black crystals of (PPh₄)₂[1⁺-(CN)₂] (20 mg, 27 %). Found: C, 71.1; H, 4.9; N, 7.1. Calc. for C₆₉H₅₆FeN₆O₅P₂: C, 71.0; H, 4.8; N, 7.2%.

5.4.6 Demetallation of 1-TAML-(X)_n for ¹H NMR Measurements

The same procedures as those described above in the Chapter 5.2.4 were employed. At specific time intervals, an aliquot (5 mL) was withdrawn, followed by the addition of pH 7 phosphate buffer solution (0.2 M, 1 mL) and aqueous sodium thiosulfate (Na₂S₂O₃, 0.2 M, 1 mL) to the aliquot, resulting in an instantaneous change in the color of the mixture from black/dark brown (depending on the reaction progress) to orange. The solvent was evaporated *in vacuo*. The dried residue was suspended in a pH 7 buffer solution (0.2 M, 1 mL) and was allowed to stir for 12 hours, during which the suspension changed from orange to beige. The suspension was filtered and the residue was washed with Et₂O (2 mL) to remove most of the N(ArMe)₃. After removing the Et₂O by filtration, the residue was suspended in DMSO-*d*₆. The suspension was filtered and one drop of concentrated hydrochloric acid (HCl, 12 N) was added to the filtrate to ensure that the TAML and the other products are not in their deprotonated forms. The solution was then characterized by ¹H NMR spectroscopy.

5.4.7 Oxidation of 1-Br in the Presence of DMOB

Compound 1,4-dimethoxybenzene (DMOB, 1.0 mg, 7.2 μmol), the Na salt of **1** (3.3 mg, 7.2 μmol), and TEABr (15 mg, 72 μmol), were dissolved in

CD₃CN (0.50 mL). The ¹H NMR spectrum of the solution was recorded. Compound (ArMe)₃N^{•+} (6.4 mg, 15 μmol) was added to the solution and was characterized by ¹H NMR spectroscopy after 5 minutes and after 24 hours with stirring.

5.4.8 Kinetics Measurements of the Reaction of Oxidized **1-Br** with Varying Concentrations of Bromide Anions

A solution of the Na salt of **1** (0.20 mM) and TEABr (2 - 14 mM) in ACN (2.0 mL) was allowed to stir for 5 minutes to form **1-Br**. (ArMe)₃N^{•+} (40 μL, 20 mM) was added to the solution and the UV-visible spectrum of the reaction mixture was recorded at 5-second intervals. Each set of kinetics data was fitted to a single exponential function and the time constant was determined by a least-squares fitting procedure in Origin. The corresponding pseudo first-order rate constant, *k_{obs}*, was derived from the reciprocal of the time constant. The second-order rate constant, *k*, for the aromatic substitution of the oxidized **1-Br** was determined from the linear fit of the plot of *k_{obs}* against Br⁻ concentration.

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Chapter 6

Anchoring of (TAML-COOH)Fe on g-C₃N₄

Photochemical activation of (TAML)Fe complex 1 resulted in catalyst modification, instead of the intended dye degradation. We proposed that having a bulky group on the phenyl ring of the TAML ligand may improve the resistance of the oxidized (TAML)Fe catalyst towards nucleophiles. Coincidentally, our carboxylate anchoring group was designed on the phenyl ring of the (TAML-COOH)Fe (3). Therefore, we proceeded to anchor 3 onto a photosensitizer. Graphitic carbon nitride (g-C₃N₄) has a suitable band structure for our envisioned photocatalysis. Hence, this chapter describes our efforts to anchor 3 onto g-C₃N₄ and subsequently evaluate its photocatalytic properties.

However, the poor performance of 3-doped g-C₃N₄ during photocatalysis suggested that the detrimental recombination of charges in g-C₃N₄ may be predominant in the presence of 3. As a result, we explored a photoelectrochemical approach to circumvent this challenge.

6.1 Introduction

From the previous chapters, we have established that the (TAML)Fe complex **1** can be photochemically oxidized by the well-known Ru(bpy)₃²⁺/Co(NH₃)₅Cl₃ system. However, the oxidized **1** intermediate (by an outer-sphere oxidant) undergoes an anion-dependent valence tautomerization, where the (TAML●⁺)Fe tautomer is susceptible to nucleophilic substitution on the TAML ligand. We believe that having a substituent on the TAML ligand, such as the –COOH group in **3**, will help to improve the stability of the oxidized intermediates. Therefore, we anchored **3** onto a photosensitizer and performed photocatalytic pollutant degradation using the composite material.

Among the photosensitizers reported,¹ we are particularly intrigued by graphitic carbon nitride (*g*-C₃N₄) due to its appealing band structure, high physiochemical stability, and its composition of earth abundant elements.² In particular, *g*-C₃N₄ has a band structure that is suitable for our application. its conduction band (CB, -1.3 V vs NHE) is comparatively more negative than most metal oxide semiconductors to perform oxygen reduction reactions, and its valence band (VB, +1.4 V vs NHE) possesses sufficient overpotential to oxidize **3** (estimated from the CV of **2** because **3** is insoluble in solvents that have sufficiently anodic potential windows).³ Furthermore, Maeda's research group has performed extensive investigations on the anchoring of metal complex catalysts onto *g*-C₃N₄ to activate the catalysts photochemically.⁴ Therefore, we set out to anchor **3** onto *g*-C₃N₄ to make a *g*-C₃N₄-**3** composite, and then evaluate its performance in photocatalytic pollutant degradation (Figure 6.1).

Figure 6.1 Reaction scheme of the photoactivation of $g\text{-C}_3\text{N}_4$ -**3** for pollutant degradation. The redox potentials of **3** featured in this figure are estimated from the CV of **2**.

6.2 Results and Discussion

By determining the amount of **3** adsorbed on g-C₃N₄ at various initial concentrations of **3** (**3**)₀, the adsorption isotherms of **3** onto g-C₃N₄ were determined (Figure 6.2a). The amount of adsorbed **3** increased with (**3**)₀. The adsorption reached its maximum at (**3**)₀ = 50 μmol g⁻¹, with a corresponding maximum adsorption of 13 μmol g⁻¹. At the same initial concentration of Ru[bpy(COOH)₂](CO)₂(Cl)₂ (50 μmol g⁻¹), almost twice as much of the Ru complex was adsorbed onto g-C₃N₄ (30 μmol g⁻¹).^{4a} Maeda *et al.* proposed that the hydrogen bonding between the -NH₂ groups on g-C₃N₄ and the electron lone pairs on the -COOH anchoring group was the attracting force binding the catalyst to the g-C₃N₄ material.^{4b} We believe that the TAML ligand may delocalize some of the electron density on the -COO⁻ groups of **3**. Consequently, the hydrogen bonding between -COO⁻ groups of **3** with g-C₃N₄ decreased, and less of **3** was adsorbed on g-C₃N₄.

We proceeded to characterize g-C₃N₄-**3**. Diffuse reflectance spectroscopic (DRS) measurements of g-C₃N₄-**3** showed an increased absorbance at the region 450 – 600 nm (blue, Figure 6.2b) compared to the spectrum of g-C₃N₄ (red, Figure 6.2b). This absorbance range coincides with the absorption bands of **3** (black, Figure 6.2b), indicating that **3** may have been adsorbed onto g-C₃N₄. Infrared (IR) spectroscopic characterization of g-C₃N₄-**3** also revealed a slightly blue-shifted band (1012 cm⁻¹, blue, Figure 6.2c), which we propose to have originated from one of the characteristic bands of **3** (1008 cm⁻¹, black, Figure 6.2c). Since the amount of **3** in g-C₃N₄-**3** is comparatively minute (13 μmol g⁻¹), DRS and IR measurements featured most of the characteristic signals from g-C₃N₄. Similarly, X-ray photoelectron spectroscopic (XPS) measurements on the Fe 3d region gave very poor signal to noise ratio. Therefore, we performed X-ray absorption spectroscopic (XAS) measurements on g-C₃N₄-**3** because better XAS

signal to noise ratio can be acquired through increased sample loading and longer measurement time. Furthermore, XAS also provides information about the coordination environment and the oxidation state of Fe of **3** before and after anchoring onto g-C₃N₄.

The Fe K-edge XAS spectra of **3** (black, Figure 6.2d), and g-C₃N₄-**3** (red, Figure 6.2d) show very similar edges, indicating that the oxidation states of Fe in **3** and g-C₃N₄-**3** are the same. This is further substantiated by the first derivative of the XAS spectra of **3** and g-C₃N₄-**3** (inset, Figure 6.2d). The pre-edge observed in the X-ray absorption near-edge structure (XANES) spectra of **3** and g-C₃N₄-**3** (* in Figure 6.2d) indicate that the Fe coordination sphere is slightly asymmetric, as observed in the 5-coordinate crystal structure of the closely related (TAML-COOMe)Fe complex **2** (Figure 3.6). Analyses of the extended X-ray absorption fine structure (EXAFS) of **3** (Figure 6.2e), and that of g-C₃N₄-**3** (Figure 6.2f) confirm that there are no significant differences in the coordination numbers and bond distances of **3** and g-C₃N₄-**3** (Table 6.1). In addition, the average Fe-O and Fe-N distances calculated from EXAFS match the values obtained from the single crystal XRD data of the closely related complex **2** (Table A.1-7 in Appendix). Taking all the data into consideration, we believe that the structure of **3** remains mostly intact before and after anchoring on g-C₃N₄, although the differences in the pre-edges (* in Figure 6.2d) suggests that g-C₃N₄ may impose additional geometrical changes on the anchored **3**, probably as a result of π - π interaction between the g-C₃N₄ and the TAML ligand.

Figure 6.2 (a) Adsorption isotherms of **3** loaded on $g\text{-C}_3\text{N}_4$. (b) Comparison of the diffuse reflectance spectra of **3** (black), $g\text{-C}_3\text{N}_4$ (red), and $g\text{-C}_3\text{N}_4\text{-3}$ (blue). (c) Comparison of the IR spectra of **3** (black), $g\text{-C}_3\text{N}_4$ (red), and $g\text{-C}_3\text{N}_4\text{-3}$ (blue). The grey dashed line features a unique IR band in **3** (1008 cm^{-1}) and this band is slightly blue-shifted in $g\text{-C}_3\text{N}_4\text{-3}$ (1012 cm^{-1} , blue). (d) Fe K-edge XAS spectra of **3** (black), and $g\text{-C}_3\text{N}_4\text{-3}$ (red). The inset shows the first derivative of the XAS spectra. The * marks the pre-edge portion of the XAS spectrum. Fits of Fe K-edge EXAFS for (e) **3**, and (f) $g\text{-C}_3\text{N}_4\text{-3}$.

Table 6.1 Fe K-edge EXAFS curve-fitting results for **3** and *g*-C₃N₄-**3**.

Sample	r (Å)	N (S ₀ ² = 0.8)	σ ² (Å ²)	E ₀ (eV)	R factor
3	1.93±0.07	5.72±0.09	0.012 ±0.009	-5.22 ±5.28	0.03
<i>g</i> -C ₃ N ₄ - 3	1.96±0.03	5.67±0.12	0.001	-10.36± 13.14	0.22

Having ascertained that **3** had been anchored on *g*-C₃N₄ to form *g*-C₃N₄-**3**, we proceeded to evaluate the photocatalytic performance of this material. Substrate *p*-cresol is suitable because it is closely related to the pollutant bisphenol-F (BPF) that we are interested in degrading. Furthermore, the simplicity of the structure of *p*-cresol would enable us to identify the products easily using ¹H NMR spectroscopy, and would help to elucidate the mechanisms involved. Subsequently, we can systematically choose substrates that possess functional groups *g*-C₃N₄-**3** is able to degrade.

The commonly reported electron acceptor for *g*-C₃N₄ is O₂, generating reactive oxygen species (ROS) such as superoxide (O₂•⁻) and H₂O₂.^{2,5} Upon light irradiation, we propose that charge separation would occur in the *g*-C₃N₄, and the hole in the valence band (VB) would oxidize **3** by *n* electrons, depending on the rate of charge transfer, to give *n*-electron oxidized intermediates of **3** (**3**^{*n*+}). We propose that **3**^{*n*+} would oxidize *p*-cresol. In the absence of **3**, as in the case of the control experiment, the hole can either participate in direct oxidation of *p*-cresol or can be used for water oxidation.² The results of photocatalytic degradation of *p*-cresol in O₂ revealed that the control experiment (*g*-C₃N₄ only) displayed a higher rate of *p*-cresol degradation compared to the experiment with *g*-C₃N₄-**3** (Figure 6.3a). We rationalized the apparent inhibitory effect of **3** as being due to the recombination of electrons in the CB with **3**^{*n*+}. If this were true, then

increasing the concentration of the electron acceptor should increase the rate of electron removal from the CB. Consequently, this may be able to outcompete the recombination process. Given that the solubility of O_2 in water at 27°C is only 37 mg/kg ($\sim 1.2\text{ mM}$),⁶ we decided to change the electron acceptor to nitrate ions (NO_3^-), since it has a higher solubility in H_2O and it has been reported as electron scavenger.⁷

Using NO_3^- (10 mM) as the electron acceptor, $g\text{-C}_3\text{N}_4\text{-3}$ performed better than $g\text{-C}_3\text{N}_4$ at photocatalytic p -cresol degradation (Figure 6.3b), supporting our hypothesis that minimizing recombination of the electrons in the CB to 3^{n+} could be the key to promote photocatalytic pollutant degradation using $g\text{-C}_3\text{N}_4\text{-3}$. However, the degradation rate of p -cresol in $g\text{-C}_3\text{N}_4\text{-3}$ with NO_3^- as the electron acceptor (black, Figure 6.3b) did not seem to be faster than that in $g\text{-C}_3\text{N}_4$ with O_2 as the electron acceptor (red, Figure 6.3a). This shows that O_2 , in comparison to NO_3^- , is a more suitable electron acceptor for $g\text{-C}_3\text{N}_4$. We believe that in order for $g\text{-C}_3\text{N}_4\text{-3}$ to work as a photocatalyst, we have to remove electrons from the CB fast enough to minimize recombination to 3^{n+} .

Figure 6.3 Photocatalytic degradation of p -cresol (0.10 mM , 20 mL) using $g\text{-C}_3\text{N}_4\text{-3}$ (5.0 mg), with (a) O_2 , and (b) NO_3^- as the sacrificial electron acceptor.

Photoelectrochemistry (PEC) is a viable option to minimize recombination of charges in $g\text{-C}_3\text{N}_4$. In principle, instead of using an electron acceptor, a small electric field, insufficient to produce Faradaic current, is applied across an electrode incorporated with $g\text{-C}_3\text{N}_4\text{-3}$. When $g\text{-C}_3\text{N}_4\text{-3}$ is irradiated with light, the charges will be separated and the electrons in the CB will flow to the cathode (containing a reductive catalyst to perform reduction reactions) due to the presence of the small electric field. In the absence of electrons in the CB, the 3^{n+} intermediates will not undergo recombination and will therefore be able to oxidize pollutants.

We incorporated $g\text{-C}_3\text{N}_4\text{-3}$ into a fluorine-doped tin oxide (FTO) glass substrate using Nafion to make an electrode, and measured the CV of $g\text{-C}_3\text{N}_4\text{-3}$, and $g\text{-C}_3\text{N}_4$. The CV showed that while $g\text{-C}_3\text{N}_4\text{-3}$ gave a higher current than $g\text{-C}_3\text{N}_4$, their onset potentials were quite similar (Figure 6.4a). It has been reported that $g\text{-C}_3\text{N}_4$ has poor charge mobility,⁸ and we proposed that the charge transfer between $g\text{-C}_3\text{N}_4$ and the FTO glass can be improved through annealing. Therefore, we annealed the FTO- $g\text{-C}_3\text{N}_4$ electrode. Since (TAML)Fe complexes are typically not stable at temperatures above 90 °C,⁹ the annealed FTO- $g\text{-C}_3\text{N}_4$ was made prior to the doping of **3**. CV measurements of the annealed electrodes revealed a four-fold increase in current and also an earlier onset potential in the presence of **3** (Figure 6.4b). When the annealed FTO- $g\text{-C}_3\text{N}_4$ electrode doped with **3** was irradiated with light, a marginally earlier onset potential (compared to the CV measured in the dark) was observed (inset, Figure 6.4c), indicating that this electrode assembly was indeed photoactive. Subsequently, we measured the photocurrents produced by the annealed FTO- $g\text{-C}_3\text{N}_4$ electrodes with and without the doping of **3**. The average photocurrent of the electrode with **3** (30 nA, red, Figure 6.4d) is higher than that without **3** (26 nA, black, Figure 6.4d). The increase in photocurrent suggests that **3** facilitates the charge separation in $g\text{-C}_3\text{N}_4$ by trapping the

hole in the Fe complex. We believe that in the presence of suitable substrates to utilize the oxidized **3**, **3** will be regenerated and the photocurrent should increase even further. Photocatalytic degradation of different substrates are ongoing using the PEC setup.

Figure 6.4 Cyclic voltammograms (scan rate = 0.1 V s^{-1}) of electrodes made of (a) FTO- $g\text{-C}_3\text{N}_4$ (black) and FTO- $g\text{-C}_3\text{N}_4\text{-3}$ without annealing, (b) annealed FTO- $g\text{-C}_3\text{N}_4$ (black) and annealed FTO- $g\text{-C}_3\text{N}_4$ doped with **3**, (c) annealed FTO- $g\text{-C}_3\text{N}_4$ doped with **3** in the dark (black) and under irradiation (red). The inset shows the expanded potentials from 1.3 to 1.5 V to highlight the earlier onset potential brought about by irradiation of light. (d) Photoelectrochemical experiments of annealed FTO- $g\text{-C}_3\text{N}_4$ (black) and annealed FTO- $g\text{-C}_3\text{N}_4$ doped with **3** (red), measured at a fixed bias of 0.40 V. $[\text{Na}_2\text{SO}_4] = 1.0 \text{ M}$.

6.3 Conclusions

In summary, we have successfully anchored **3** on $g\text{-C}_3\text{N}_4$ as a photosensitizer, and characterized the $g\text{-C}_3\text{N}_4\text{-3}$ composite using DRS, IR spectroscopic, and XAS measurements. Photocatalytic degradation of *p*-cresol revealed that the presence of **3** in $g\text{-C}_3\text{N}_4$ did not result in a significant improvement in comparison to the control experiments ($g\text{-C}_3\text{N}_4$ without **3**). We proposed that **3**, after being oxidized by the hole(s) from the VB of $g\text{-C}_3\text{N}_4$, might have recombined faster with the electrons in the CB. This hypothesis was substantiated by the improved performance of *p*-cresol degradation in $g\text{-C}_3\text{N}_4\text{-3}$, when a NO_3^- electron acceptor (10 mM) at a larger concentration than O_2 electron acceptor (<1.2 mM), was used. To further minimize the effect of charge recombination, we adopted a photoelectrochemical approach and used an electric field instead of a chemical electron acceptor. We also improved the poor interfacial charge transfer from $g\text{-C}_3\text{N}_4$ to the FTO electrode by annealing the $g\text{-C}_3\text{N}_4$ onto FTO glass before doping it with **3**. Preliminary evaluations of the electrodes using CV and photoelectrical experiments showed that the doping of the annealed FTO- $g\text{-C}_3\text{N}_4$ electrode with **3** lowered the onset potential and increased the amount of photocurrent. These promising results have propelled us to explore the photoelectrocatalytic degradation of pollutants.

6.4 Materials and Methods

6.4.1 General Information

Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry (TCI). Unless otherwise stated, the commercial reagents were used as purchased. Fluorine-doped tin oxide (FTO)-coated glass slide (surface resistivity $\sim 3 \times 10^{-4} \Omega\text{m}$) was purchased from Sigma-Aldrich. A ThermolyneTM furnace (Thermo Fischer Scientific) was used for calcination reactions. UV-visible absorption measurements were carried out on a Shimadzu UV-3600 spectrophotometer. Photochemical and photoelectrochemical measurements were performed using a CHI 660E potentiostat (CH Instruments Inc.) and the sample was irradiated with a 300 W Xenon lamp (Newport Corporation) equipped with a cutoff filter (≥ 420 nm). The distance between the electrochemical cell and the lamp was adjusted to ensure that the light intensity on the surface of electrode is fixed at 100 mW/cm^2 . The light intensity was measured using a silicon photodiode (13 DAS 005, Melles Griot) connected to a broad-band power/energy meter (13 PEM 001, Melles Griot).

X-ray absorption fine structure (XAFS) characterization at the Fe K-edge was carried out at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS).³⁷ All XAS measurements were collected with a ring energy of 0.7 GeV and a ring current of ca. 200 mA. A Si(111) crystal monochromator was used and the data were collected in transmission mode at ambient temperatures. The X-ray energy was calibrated at the inflection point of the absorption edge of a nickel foil. Data analysis was carried out with the programs Athena and Artemis included in the Demeter package (version 0.9.25). Each of the powder samples was prepared as a pellet using a pelletizer of diameter 10 mm and mounted on the sample holder for the

XAS measurement. ARTEMIS fittings were carried out with *k*-weight = 1,2,3; *k* range = 3 – 12.69, and *R* range = 1 – 3 Å.

6.4.2 Synthesis of Graphitic Carbon Nitride (*g*-C₃N₄)

Urea (CH₄N₂O, 3.0 g, 50 mmol) was calcined to give *g*-C₃N₄ by first heating it in a furnace at 550 °C at a ramp rate of 5.0 °C min⁻¹. Subsequently, the furnace's temperature was maintained at 550 °C for a further 2 hours. Light yellow *g*-C₃N₄ (0.86 g, 9.0%) was obtained and was ground into a powder using a mortar and a pestle.

6.4.3 Anchoring of **3** on *g*-C₃N₄

The procedures for anchoring **3** on *g*-C₃N₄ have been adopted from those reported by Maeda's research group.^{4a,4c} A stock solution of **3** (0.30 mM, 20 mg in 100 mL MeOH) was prepared. The *g*-C₃N₄ (20 mg) was transferred into a Schlenk flask containing a solution of **3** (10 mL). The suspension was sonicated for 15 minutes, resulting in a pale orange suspension. The suspension was stirred at room temperature for 24 hours. The resulting reaction mixture was centrifuged at 14000 rpm for 10 minutes, after which the supernatant containing unanchored **3** was removed. The remaining sediment (*g*-C₃N₄-**3**) was suspended in MeOH (10 mL), sonicated for 15 minutes, and then centrifuged at 14000 rpm for 10 minutes. This process was repeated twice to ensure that all the unanchored **3** was removed. The purified *g*-C₃N₄-**3** was dried *in vacuo* for 4 hours at room temperature.

6.4.4 Determination of the Adsorption Isotherms of **3** on *g*-C₃N₄

All the supernatant fractions containing unanchored **3** from the purification of *g*-C₃N₄-**3** in section 6.4.3 were combined and concentrated using rotary evaporation.

The concentrated solution was transferred into a 10 mL volumetric flask and diluted with MeOH to make a 10 mL solution. UV-visible spectroscopic measurements on the solution were then performed. The decrease in absorbance at the 455 nm absorption band in comparison to that of the solution of **3** before anchoring was calculated, and the percentage of decrease was then converted into the amount of **3** loaded on $g\text{-C}_3\text{N}_4$ ($\mu\text{mol g}^{-1}$). The adsorption isotherms of **3** loaded on $g\text{-C}_3\text{N}_4$ were used to determine the amount of **3** loaded on $g\text{-C}_3\text{N}_4$ at different initial concentrations of **3**.

6.4.5 Photocatalytic Degradation of *p*-Cresol Using $g\text{-C}_3\text{N}_4\text{-3}$

With O_2 as the electron acceptor. Composite material $g\text{-C}_3\text{N}_4\text{-3}$ (5 mg) was suspended in *p*-cresol solution in H_2O (0.10 mM, 10 mL) in a 25 mL one-arm sealed tube. The suspension was sonicated for 15 minutes and the suspension was stirred for 12 hours in the dark. Subsequently, the suspension was bubbled with O_2 for 15 minutes. The tube was sealed with a Teflon cap and the side arm was connected to a balloon containing O_2 . The suspension was irradiated with visible light from a white LED (48 W). At intervals of one hour, 3 mL aliquots were drawn from the suspension. Each aliquot was centrifuged at 14000 rpm for 10 minutes, and the supernatant was collected. The supernatant was then centrifuged again at 14000 rpm for 10 minutes to remove most of the solid materials. The resulting supernatant was transferred into a 1 mL volumetric flask containing a 1,4-dinitrobenzene internal standard solution (10 mM, 0.010 mL) to make up a 1 mL solution. The solution was then analyzed using high performance-liquid chromatography (HPLC) and the concentration of *p*-cresol was determined. The control experiments were performed using $g\text{-C}_3\text{N}_4$ in place of $g\text{-C}_3\text{N}_4\text{-3}$.

With nitrate (NO_3^-) as the sacrificial electron acceptor. The same protocol as the previous section was adopted. After the suspension was stirred in the dark for

12 hours, potassium nitrate (KNO₃, 10 mg, 0.010 mmol) was added to the *p*-cresol solution to give [KNO₃] = 10 mM. Instead of O₂, the suspension was bubbled with N₂ gas for 15 minutes to remove the dissolved O₂.

6.4.6 Photoelectrochemical Experiments

Complex **3** and *g*-C₃N₄ were incorporated into a fluorine-doped tin oxide (FTO)-coated glass slide to make an electrode. The FTO coated glass slides were sonicated in acetone for 30 minutes and the acetone was decanted. This process was repeated using EtOH, and then ultrapure water. The treated FTO-coated glass slides were left to dry in air for 12 h. The dried FTO-coated glass slides were layered with Parafilm sheets with 3.1 mm² openings. Two methods were applied to make the FTO electrodes.

Without annealing. Material *g*-C₃N₄ or *g*-C₃N₄-**3** (3.0 mg), and Nafion (0.020 mL) were suspended in ultrapure water (1.0 mL). The suspension (0.015 mL) was then drop-cast onto the treated FTO-coated glass and left to dry in air for 12 hours. This step was repeated four times.

With annealing. Material *g*-C₃N₄ (3.0 mg) and Nafion (0.020 mL) were suspended in ultrapure water (1.0 mL). The suspension (0.015 mL) was then drop-cast onto the treated FTOcoated glass and left to dry in air for 12 hours. This step was repeated four times. The FTO-coated glass slide was then placed in a furnace and was annealed at 200 °C for 2 hours under a N₂ atmosphere. Upon cooling down, the annealed FTO-*g*-C₃N₄ electrode was doped with **3** by immersing the annealed FTO-*g*-C₃N₄ electrode in a solution of **3** (0.30 mM, 10 mL) for 2 hours and then left to dry in air for 12 hours.

The photoelectrochemical cell was set up using a similar configuration as a standard three-electrode electrochemical cell, with each of the electrodes

described above as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl reference electrode. The setup was connected to a potentiostat and light from a Xe lamp was oriented to irradiate the working electrode. Cyclic voltammetry was performed on all the electrodes. The photoelectrochemical properties of the electrodes were evaluated by measuring the photocurrent produced during irradiation at a fixed bias of 0.40 V vs Ag/AgCl.

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Chapter 7

Discussion and Future Work

This chapter recaps the findings from previous chapters and the new understanding about the photochemical activation of (TAML)Fe complexes. A thorough review of the overall work in the context of the thesis hypothesis is given. Finally, this chapter describes future work to extend our understanding of the photochemical activation of (TAML)Fe complexes.

7.1 General Discussion

7.1.1 Synthesis of (TAML)Fe Complexes

In the first part of the chapter, the synthesis of the previously reported (TAML)Fe (**1**) was described. The reported main precursor used in the synthetic route for (TAML)Fe complexes, *o*-phenylenediamines has a limited choice of substituted analogs that are commercially available. In order for us to introduce anchoring groups on the ligand, we had to reevaluate the entire synthetic route to replace *o*-phenylenediamines with a more precursor with more commercially available substituted analogs. Therefore, we have proposed a new approach that utilizes nitroaniline precursors instead of *o*-phenylenediamine precursors, enabling the syntheses of new (TAML-COOMe)Fe (**2**) and (TAML-COOH)Fe (**3**) complexes. Various challenges and findings encountered during this endeavor, in particular the intramolecular condensation and ester hydrolysis of **2** to form **3**, have been reported. The synthetic intermediates and products have been characterized by ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and single crystal X-ray diffraction analysis.

The success of the new synthetic route has been the key to obtain the first (TAML)Fe complex containing a carboxylate anchoring group, (TAML-COOH)Fe (**3**). Having an anchoring group opens up new opportunities to bind (TAML)Fe complexes on semiconductor materials containing hydroxyl groups such as metal oxides, and materials that can form hydrogen bonding such as graphitic carbon nitride. In dye-sensitized solar cells (DSSCs), anchoring groups have been reported to increase electron transfer kinetics and improve the stability of the molecular photosensitizer.¹ Therefore, our new synthetic route can be used to develop (TAML)Fe complexes with other anchoring group, and may be incorporated into the synthetic routes of other generations of (TAML)Fe complexes.

7.1.2 Characterization of (TAML)Fe Complexes

To characterize the electrochemical properties complexes **1** and **2**, cyclic voltammetry experiments have been performed. Contrary to the single redox potential of $E_{1/2} = 0.50$ V vs Fc^+/Fc , we discovered that **1** has three quasi-reversible redox waves. Based on the change in CV after one scan, and the shapes of the CV waves, we proposed that the oxidized **1** intermediates underwent non-electron transfer (ET) reactions that resulted in the modification of **1**. In other words, the photochemically oxidized **1** may undergo non ET reactions. Nonetheless, the redox potentials of all the three waves are less positive than that of $\text{Ru}(\text{bpy})_3^{3+}$, suggesting that $\text{Ru}(\text{bpy})_3^{2+}$ should be a suitable photosensitizer to oxidize **1** photochemically. The CV data of a (bTAML)Fe complex, which can be photochemically activated, shows two quasi-reversible waves at 0.42 V and 0.97 V vs Ag/AgCl. They assigned these two waves to the $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{V}}/\text{Fe}^{\text{IV}}$ redox couples.² More interestingly, they also reported a third irreversible wave at around 1.5 V vs Ag/AgCl, which they assigned to a ligand oxidation event.² It is possible that since **1** has a more conjugated ligand structure, the ligand oxidation potential may have been lowered. Therefore, we may expect the photochemically oxidized **1** to be ligand-based.

As a proof of concept that (TAML)Fe complexes can be photochemically activated by a $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system, we characterized the photophysical properties of **1** using transient absorption spectroscopic (TAS) experiments. The TAS results have verified that the $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system is able to oxidize **1** by at least one electron, producing a relatively long-lived oxidized **1** intermediate. This intermediate was corroborated using UV-visible spectroscopic measurements of **1** oxidized by independently generated $\text{Ru}(\text{bpy})_3^{3+}$. These results concur with the mechanisms proposed by Panda *et. al.*, when they used a $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ photosensitizer system to perform water oxidation.²

On the other hand, motivated by the possibility of assessing the rarely reported three-electron oxidized **2** (formally Fe^{VI} complex), we oxidized **2** electrochemically and chemically at low temperature ($-80\text{ }^{\circ}\text{C}$). The preliminary results indicate that the three-electron oxidized **2** (2^{3+}) may have been generated, and efforts to characterize this intermediate spectroscopically and by X-ray crystallography are still ongoing. Preliminary kinetics experiments of the reactivity of 2^{3+} in the oxidation of *p*-substituted thioanisoles have shown the electrophilic nature of this reaction. However, the kinetics data have suggested that other competing reactions may have occurred during the kinetics measurements. Therefore, the experimental procedures are being examined, in hopes of obtaining more accurate kinetics data of the reactivity of 2^{3+} towards various substrates. The ability to access to 2^{3+} has a high impact on the way (TAML)Fe has been understood, that the (TAML)Fe^V(O) is the reactive intermediate, while in fact, a formally Fe^{VI} complex may display a higher reactivity. We believe this is due to the more conjugated ligand system of **2** compared to other generations of (TAMLL)Fe reported so far.

7.1.3 Anion-Dependent Valence Tautomerisation

Although the photophysical and electrochemical properties of **1** suggested that **1** can be oxidized by $\text{Ru}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_5\text{Cl}_3$ photosensitizer system, the photocatalyst system did not translate into higher rate of dye degradation. In fact, an inhibitory effect was observed in the presence of **1**. To understand the underlying reasons for these unexpected results, we performed mechanistic studies, kinetics measurements, mass spectrometry analysis, and Mössbauer spectroscopy, we showed that ligand-based oxidation occurred to give **1-TAML•⁺** in equilibrium with the (TAML)Fe^{IV} counterpart. The extent of valence tautomerization depends on the exogenous anions present. A strongly-coordinating CN^- will become an axial ligand to stabilize Fe^{IV} , and we have isolated and structurally

characterized an unprecedented dicyano (TAML)Fe^{IV} complex. On the other hand, labile halides favor the Fe^{III} **1-TAML•**⁺ tautomer, which is susceptible to nucleophilic substitution on the ligand. Similar nucleophilic reactions could arise in other Fe complexes, especially under harsh pollutant degradation, water oxidation, or C-H activation conditions, leading to catalyst modification.

From a broader perspective, our findings highlight some of the important aspects for developing photodriven biomimetic oxidation catalysts and an uncommon mechanism for high-valent iron reactivity. Currently, the most common oxidants to access high-valent iron species are inner-sphere reagents like peroxides or hypervalent iodine reagents. We report the generation of this unique **1-TAML•**⁺ rather than the established (TAML)Fe^{IV} or Fe^V motifs, by using photochemically produced Ru(bpy)₃³⁺. Although valence tautomerization is observed in some synthetic porphyrinoid counterparts,³ anion-dependent valence tautomerization in non-heme iron systems are uncommon.⁴ Most significantly, the reported radical-cations often show enhanced substrate C-H activation behavior,⁵ similar to reports on cytochrome P450, and recently on Mn^{IV}(O-LA)(TBP8Cz•⁺) (LA = Lewis acid, TBP8Cz = octakis(p-tert-butylphenyl)corrolazinato³⁻) as well.^{3b} However, we show that radical-cations on sterically unprotected ligands are susceptible to nucleophilic attack. These insights should be valuable in future studies and designs of biomimetic high valent catalysts.

7.1.4 Anchoring of (TAML-COOH)Fe on *g*-C₃N₄

Having ascertained that the TAML ligand of oxidized **1** can result in ligand modification, and the modification mechanism is through a nucleophilic substitution, we proposed that putting substituents on the ligand may hinder

nucleophiles from attacking the ligand-based oxidized intermediate. This feature coincided with the (TAML)Fe complex **3** bearing $-\text{COOH}$ anchoring groups that happened to be at the aryl ring of the ligand. Therefore, we proceeded to anchor **3** on $g\text{-C}_3\text{N}_4$ as a photosensitizer. Characterization of the $g\text{-C}_3\text{N}_4\text{-3}$ composite using DRS, IR spectroscopic, and XAS measurements are convincing, that the presence of $-\text{COOH}$ group had enabled the anchoring of (TAML)Fe complexes on $g\text{-C}_3\text{N}_4$. This finding agrees with our hypothesis that a hybrid heterogeneous light absorbing material-(TAML)Fe catalyst, such as those reported for DSPEC, can be formed via the introduction of anchoring groups on the Fe catalyst.

However, photocatalytic degradation of *p*-cresol revealed that the presence of **3** in $g\text{-C}_3\text{N}_4$ did not result in a significant improvement in comparison to the control experiments ($g\text{-C}_3\text{N}_4$ without **3**). We proposed that **3**, after being oxidized by the hole(s) from the VB of $g\text{-C}_3\text{N}_4$, might have recombined faster with the electrons in the CB. This hypothesis was substantiated by the improved performance of *p*-cresol degradation in $g\text{-C}_3\text{N}_4\text{-3}$, when a NO_3^- electron acceptor (10 mM) at a larger concentration than O_2 electron acceptor (<1.2 mM), was used. This finding implies that in the event the photoredox reactions do not occur faster than the charge recombination, then the hybrid $g\text{-C}_3\text{N}_4\text{-3}$ system would not perform the degradation reactions that we desire.

To further minimize the effect of charge recombination, we adopted a photoelectrochemical approach and used an electric field instead of a chemical electron acceptor. We also improved the poor interfacial charge transfer from $g\text{-C}_3\text{N}_4$ to the FTO electrode by annealing the $g\text{-C}_3\text{N}_4$ onto FTO glass before doping it with **3**. Preliminary evaluations of the electrodes using CV and photoelectrical experiments showed that the doping of the annealed FTO- $g\text{-C}_3\text{N}_4$ electrode with **3** lowered the onset potential and

increased the amount of photocurrent. These promising results have propelled us to explore the photoelectrocatalytic degradation of pollutants.

7.2 Outstanding Questions and Future Work

The development of (TAML)Fe complexes was pioneered by Collins' research group since the 1980s.⁶ The report on the rapid destruction of chlorophenols in 2002 uncovered the potential of using (TAML)Fe complexes as water treatment catalysts.⁷ At the start of this Ph.D. project, we were intrigued by the rare reports of photochemical activation of (TAML)Fe complexes, since there is an evolution in the literature to move away from chemical oxidants to more practical activation methods such as using O_2 ,⁸ electrochemistry,⁹ and biological enzymes.¹⁰ We realized that there was no in-depth study of the photophysics of the photochemical activation of (TAML)Fe complexes using photosensitizers. Therefore, we hypothesized that, with better understanding of the photophysical and electrochemical properties, we can design a photochemical system that can transfer the hole generated from photoexcitation to the (TAML)Fe catalyst, resulting in photochemical activation of the catalyst.

Through the discovery of the anion-dependent valence tautomerization in oxidized (TAML)Fe complex **1**, we gained more understanding about the photochemically oxidized **1** intermediate, and that this intermediate can undergo other side reactions. Therefore, we proposed that the anchoring group will not only increase the charge transfer rate between the excited photosensitizer and the (TAML)Fe catalyst, it will also serve as a bulky group to protect the aryl ring of the TAML ligand. In addition, by incorporating (TAML)Fe catalyst into a light absorbing semiconductor material in our rendition of a heterogeneous photocatalyst, the immobilized Fe catalyst may gain more stability. From the research results obtained so far, it is evident that more work needs to be done to achieve our objectives.

From the perspective of anchoring group incorporation into (TAML)Fe complexes. We will explore other anchoring groups that possess greater charge

transfer properties and higher affinity to the photosensitizer. Some possible anchoring groups that we will explore include hydroxamates,¹¹ and phosphonates.¹² Subsequently, we will incorporate the (TAML)Fe complexes with the new anchoring group into photosensitizers and compare their performances in photocatalytic pollutant degradation.

Another interesting project that we will pursue is the characterization of the possibly formally $\text{Fe}^{\text{VI}} \mathbf{2}^{3+}$ intermediate. Spectroscopic and crystallographic characterizations are ongoing. We will also study the stability and the reactivity of the $\mathbf{2}^{3+}$ intermediate.

Finally, we have recently embarked on our envisioned hybrid photocatalyst system that incorporates a (TAML)Fe complex into a light absorbing semiconductor material for a heterogeneous photocatalytic pollutant degradation. The preliminary results with the spectroelectrochemical activation of FTO-g- C_3N_4 -**3** seemed promising. We are currently investigating the reactivity of the hybrid material in the oxidation of known substrates such as benzyl alcohols,¹³ bisphenols,¹⁴ and hydrocarbons.¹⁵

In conclusion, the objective of my Ph.D. thesis is to activate (TAML)Fe complexes photochemically for pollutant degradation. Through thorough photophysical and electrochemical characterizations of (TAML)Fe complex **1**, we have shown that **1** can be photochemically oxidized. However, the photochemically oxidized **1** undergoes an exogenous anion-dependent valence tautomerization, which leads to the C-H activation and nucleophilic substitution in the TAML ligand. This ligand modification pathway illustrates one of the possible ways that a photochemically oxidized (TAML)Fe complex can undergo side reactions, instead of the intended pollutant degradation. Therefore, while this research project succeeds in understanding and oxidizing (TAML)Fe complexes photochemically, it has yet to succeed in utilizing the photochemically oxidized

(TAML)Fe complexes to perform pollutant degradation. To realize this objective, we are currently exploring the photoelectrocatalytic degradation of pollutants using the hybrid $g\text{-C}_3\text{N}_4$ -**3** photocatalyst system.

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APPENDIX

NMR Spectra **Figure A.1** The ^1H and ^{13}C NMR spectra of ligand precursor **1A**.

Figure A.2 The ^1H and ^{13}C NMR spectra of ligand precursor **1B**.

Figure A.3 The ^1H and ^{13}C NMR spectra of ligand precursor **1C**.

Figure A.4 The ^1H and ^{13}C NMR spectra of ligand precursor **1D**.

Figure A.5 The ^1H and ^{13}C NMR spectra of ligand precursor **2A**. The inset shows an expanded range of the aromatic region.

Figure A.6 The ^1H and ^{13}C NMR spectra of ligand precursor **2B**. The inset shows an expanded range of the aromatic region.

Figure A.7 The ^1H and ^{13}C NMR spectra of ligand precursor **2C**. The inset shows an expanded range of the aromatic region.

Figure A.8 The ^1H and ^{13}C NMR spectra of ligand precursor **2D**. The inset shows an expanded range of the aromatic region.

Figure A.9 The ^1H spectrum of demetalated **3**. The inset shows an expanded range of the aromatic region.

Figure A.10 The ^1H spectrum of TAML-COOH (hydrolysed from **2D**). The inset shows an expanded range of the aromatic region.

Figure A.11 The ¹H spectrum of [Ar(Br)₂]₃N. The inset shows an expanded range of the aromatic region.

Figure A.12 The ¹H spectrum of (ArMe)₃N.

X-ray Crystallographic Data of 2**Table A.1** Crystal data for **2**.

Identification code	shs144s	
Chemical formula	C ₄₉ H ₄₅ FeN ₅ O ₁₀ P	
Formula weight	950.72 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.160 x 0.320 mm	
Crystal habit	red needle	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 21.2318(15) Å	$\alpha = 90^\circ$
	b = 21.7767(16) Å	$\beta = 94.205(2)^\circ$
	c = 19.1738(14) Å	$\gamma = 90^\circ$
Volume	8841.3(11) Å ³	
Z	8	
Density (calculated)	1.428 g/cm ³	
Absorption coefficient	0.445 mm ⁻¹	
F(000)	3960	

Table A.2 Data collection and structure refinement for **2**.

Theta range for data collection	1.34 to 27.00°	
Index ranges	-27<= <i>h</i> <=27, -27<= <i>k</i> <=27, -24<= <i>l</i> <=24	
Reflections collected	67433	
Independent reflections	9654 [R(int) = 0.0847]	
Coverage of independent reflections	100.0%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9490 and 0.8710	
Structure solution technique	direct methods	
Structure solution program	XS, VERSION 2013/1	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9654 / 116 / 641	
Goodness-of-fit on F ²	1.013	
$\Delta/\sigma_{\max}$	0.002	
Final R indices	6634 data; I>2σ(I)	R1 = 0.0487, wR2 = 0.1131
	all data	R1 = 0.0821, wR2 = 0.1354
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0524P)^2+22.7382P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	

Largest diff. peak and hole	0.741 and -0.744 eÅ ⁻³
R.M.S. deviation from mean	0.079 eÅ ⁻³

Table A.3 Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for **2**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Fe1	0.05631(2)	0.74914(2)	0.60513(2)	0.01305(11)
C1	0.07834(12)	0.78392(12)	0.74282(13)	0.0116(5)
C2	0.07639(11)	0.71288(12)	0.74326(13)	0.0112(5)
C3	0.09987(13)	0.80800(12)	0.48142(14)	0.0168(6)
C4	0.07849(13)	0.74849(12)	0.44189(13)	0.0146(5)
C5	0.09642(12)	0.68832(12)	0.48160(13)	0.0133(5)
C6	0.00576(13)	0.74993(13)	0.42804(14)	0.0197(6)
C7	0.10780(15)	0.74734(13)	0.37138(14)	0.0208(6)
C8	0.07730(12)	0.86719(12)	0.65606(13)	0.0127(5)
C9	0.08584(12)	0.87212(12)	0.58356(13)	0.0124(5)
C10	0.09521(12)	0.93034(12)	0.55586(14)	0.0160(6)
C11	0.09493(12)	0.98176(12)	0.59859(14)	0.0167(6)
C12	0.08438(12)	0.97648(12)	0.66941(14)	0.0141(5)
C13	0.07588(12)	0.91859(12)	0.69861(14)	0.0140(6)
C14	0.08492(13)	0.03318(13)	0.71234(14)	0.0182(6)
C15	0.08219(18)	0.07322(14)	0.82685(16)	0.0331(8)
C16	0.07215(12)	0.62967(12)	0.65509(13)	0.0118(5)
C17	0.07547(12)	0.62464(12)	0.58168(13)	0.0130(5)
C18	0.07651(12)	0.56649(12)	0.55136(14)	0.0158(6)
C19	0.07560(13)	0.51478(12)	0.59362(14)	0.0174(6)
C20	0.07382(12)	0.51986(12)	0.66600(14)	0.0142(6)
C21	0.07170(12)	0.57756(12)	0.69742(13)	0.0130(5)
C22	0.07674(12)	0.46263(12)	0.70764(14)	0.0152(6)
C23	0.07988(15)	0.41939(13)	0.82084(15)	0.0237(7)
C24	0.31185(12)	0.89512(12)	0.96494(14)	0.0156(6)
C25	0.36788(13)	0.86191(13)	0.97671(14)	0.0184(6)
C26	0.41188(13)	0.87946(13)	0.03004(15)	0.0210(6)
C27	0.40017(14)	0.92890(14)	0.07203(15)	0.0233(7)
C28	0.34468(14)	0.96173(14)	0.06121(15)	0.0236(7)
C29	0.30033(13)	0.94519(13)	0.00771(15)	0.0201(6)
C30	0.17870(12)	0.88134(12)	0.93182(14)	0.0157(6)
C31	0.12932(12)	0.91463(12)	0.89857(14)	0.0158(6)
C32	0.07205(13)	0.91832(13)	0.92882(14)	0.0181(6)
C33	0.06413(13)	0.88940(13)	0.99179(15)	0.0189(6)

C34	0.11365(13)	0.85642(13)	0.02570(15)	0.0204(6)
C35	0.17106(13)	0.85233(13)	0.99592(15)	0.0187(6)
C36	0.25522(12)	0.92860(13)	0.82314(15)	0.0187(6)
C37	0.26711(14)	0.99065(14)	0.83479(18)	0.0270(7)
C38	0.26468(15)	0.03054(16)	0.77809(19)	0.0343(8)
C39	0.25129(15)	0.00876(17)	0.71110(19)	0.0360(9)
C40	0.23938(15)	0.94722(17)	0.69948(17)	0.0330(8)
C41	0.24120(14)	0.90676(15)	0.75570(15)	0.0243(7)
C42	0.26680(13)	0.79993(13)	0.86350(14)	0.0166(6)
C43	0.22282(13)	0.75341(13)	0.87085(15)	0.0189(6)
C44	0.23462(14)	0.69472(13)	0.84663(16)	0.0229(6)
C45	0.29035(14)	0.68272(14)	0.81550(15)	0.0242(7)
C46	0.33386(14)	0.72920(14)	0.80688(15)	0.0237(7)
C47	0.32259(13)	0.78822(13)	0.83018(14)	0.0194(6)
N1	0.06919(10)	0.80609(10)	0.67744(11)	0.0125(5)
N2	0.06940(10)	0.69105(10)	0.67727(11)	0.0121(5)
N3	0.07272(10)	0.68190(10)	0.54586(11)	0.0123(5)
N4	0.07865(10)	0.81550(10)	0.54669(11)	0.0132(5)
O1	0.08981(9)	0.81364(8)	0.79737(9)	0.0162(4)
O2	0.08233(8)	0.68325(8)	0.79832(9)	0.0142(4)
O3	0.13269(11)	0.84566(10)	0.45322(11)	0.0318(6)
O4	0.12899(10)	0.64974(9)	0.45474(10)	0.0230(5)
O5	0.09029(10)	0.08467(9)	0.69057(11)	0.0260(5)
O6	0.07918(10)	0.02084(9)	0.78053(10)	0.0251(5)
O7	0.08129(10)	0.41139(9)	0.68364(10)	0.0226(5)
O8	0.07451(9)	0.47311(8)	0.77658(10)	0.0192(4)
O9	0.95731(9)	0.75090(9)	0.59610(9)	0.0148(4)
O10	0.24859(14)	0.58140(14)	0.49030(19)	0.0639(9)
P1	0.25364(3)	0.87611(3)	0.89520(4)	0.01493(16))
N5	0.2891(5)	0.7196(7)	0.3328(9)	0.093(4)
C48	0.2838(12)	0.7631(7)	0.3637(11)	0.071(4)
C49	0.2648(8)	0.8162(8)	0.4030(9)	0.081(4)
N5A	0.2811(4)	0.6997(4)	0.3914(8)	0.111(4)
C48A	0.2761(6)	0.7522(5)	0.3804(8)	0.062(3)
C49A	0.2708(4)	0.8188(4)	0.3701(5)	0.046(2)

Table A.4 Bond lengths (Å) for **2**.

Fe1-N1	1.865(2)	Fe1-N2	1.880(2)
Fe1-N3	1.901(2)	Fe1-N4	1.910(2)
Fe1-O9	2.0967(19)	C1-O1	1.239(3)
C1-N1	1.344(3)	C1-C2	1.548(4)

C2-O2	1.236(3)	C2-N2	1.349(3)
C3-O3	1.227(3)	C3-N4	1.371(3)
C3-C4	1.552(4)	C4-C7	1.529(3)
C4-C6	1.548(4)	C4-C5	1.549(4)
C5-O4	1.225(3)	C5-N3	1.372(3)
C8-C13	1.387(4)	C8-N1	1.406(3)
C8-C9	1.419(3)	C9-C10	1.394(4)
C9-N4	1.424(3)	C10-C11	1.388(4)
C11-C12	1.397(4)	C12-C13	1.396(4)
C12-C14	1.484(4)	C14-O5	1.205(3)
C14-O6	1.349(3)	C15-O6	1.444(3)
C16-C21	1.395(4)	C16-N2	1.405(3)
C16-C17	1.419(3)	C17-C18	1.394(4)
C17-N3	1.423(3)	C18-C19	1.388(4)
C19-C20	1.396(4)	C20-C21	1.396(4)
C20-C22	1.479(4)	C22-O7	1.214(3)
C22-O8	1.346(3)	C23-O8	1.445(3)
C24-C25	1.396(4)	C24-C29	1.397(4)
C24-P1	1.801(3)	C25-C26	1.387(4)
C26-C27	1.378(4)	C27-C28	1.381(4)
C28-C29	1.388(4)	C30-C31	1.390(4)
C30-C35	1.402(4)	C30-P1	1.789(3)
C31-C32	1.387(4)	C32-C33	1.383(4)
C33-C34	1.394(4)	C34-C35	1.386(4)
C36-C41	1.389(4)	C36-C37	1.390(4)
C36-P1	1.795(3)	C37-C38	1.389(4)
C38-C39	1.379(5)	C39-C40	1.379(5)
C40-C41	1.390(4)	C42-C43	1.392(4)
C42-C47	1.410(4)	C42-P1	1.796(3)
C43-C44	1.389(4)	C44-C45	1.389(4)
C45-C46	1.388(4)	C46-C47	1.387(4)
N5-C48	1.128(14)	C48-C49	1.453(14)
N5A-C48A	1.167(11)	C48A-C49A	1.466(11)

Table A.5 Bond angles (°) for **2**.

N1-Fe1-N2	83.96(9)	N1-Fe1-N3	158.91(10)
N2-Fe1-N3	84.14(9)	N1-Fe1-N4	84.48(9)
N2-Fe1-N4	155.68(10)	N3-Fe1-N4	99.66(9)
N1-Fe1-O9	98.08(8)	N2-Fe1-O9	99.58(8)
N3-Fe1-O9	101.03(8)	N4-Fe1-O9	103.19(8)
O1-C1-N1	127.3(2)	O1-C1-C2	121.4(2)
N1-C1-C2	111.2(2)	O2-C2-N2	127.9(2)

O2-C2-C1	121.7(2)	N2-C2-C1	110.4(2)
O3-C3-N4	123.9(3)	O3-C3-C4	119.9(2)
N4-C3-C4	116.2(2)	C7-C4-C6	108.3(2)
C7-C4-C5	108.6(2)	C6-C4-C5	107.9(2)
C7-C4-C3	108.8(2)	C6-C4-C3	108.6(2)
C5-C4-C3	114.4(2)	O4-C5-N3	124.3(2)
O4-C5-C4	120.0(2)	N3-C5-C4	115.8(2)
C13-C8-N1	125.7(2)	C13-C8-C9	121.7(2)
N1-C8-C9	112.6(2)	C10-C9-C8	118.3(2)
C10-C9-N4	127.7(2)	C8-C9-N4	113.8(2)
C11-C10-C9	120.1(2)	C10-C11-C12	121.0(2)
C13-C12-C11	119.9(2)	C13-C12-C14	121.7(2)
C11-C12-C14	118.4(2)	C8-C13-C12	118.9(2)
O5-C14-O6	122.6(3)	O5-C14-C12	125.4(3)
O6-C14-C12	112.0(2)	C21-C16-N2	126.5(2)
C21-C16-C17	121.1(2)	N2-C16-C17	112.3(2)
C18-C17-C16	119.2(2)	C18-C17-N3	126.6(2)
C16-C17-N3	114.1(2)	C19-C18-C17	119.5(2)
C18-C19-C20	121.2(2)	C19-C20-C21	120.3(2)
C19-C20-C22	117.8(2)	C21-C20-C22	121.8(2)
C16-C21-C20	118.6(2)	O7-C22-O8	122.5(2)
O7-C22-C20	124.9(2)	O8-C22-C20	112.6(2)
C25-C24-C29	119.6(3)	C25-C24-P1	122.1(2)
C29-C24-P1	118.4(2)	C26-C25-C24	119.7(3)
C27-C26-C25	120.4(3)	C26-C27-C28	120.3(3)
C27-C28-C29	120.1(3)	C28-C29-C24	119.9(3)
C31-C30-C35	120.3(2)	C31-C30-P1	121.0(2)
C35-C30-P1	118.6(2)	C32-C31-C30	119.5(3)
C33-C32-C31	120.3(3)	C32-C33-C34	120.4(3)
C35-C34-C33	119.8(3)	C34-C35-C30	119.6(3)
C41-C36-C37	120.4(3)	C41-C36-P1	118.9(2)
C37-C36-P1	120.6(2)	C38-C37-C36	119.1(3)
C39-C38-C37	120.5(3)	C40-C39-C38	120.5(3)
C39-C40-C41	119.7(3)	C36-C41-C40	119.8(3)
C43-C42-C47	120.4(3)	C43-C42-P1	121.1(2)
C47-C42-P1	118.5(2)	C44-C43-C42	119.8(3)
C45-C44-C43	119.8(3)	C46-C45-C44	120.6(3)
C47-C46-C45	120.3(3)	C46-C47-C42	119.0(3)
C1-N1-C8	126.8(2)	C1-N1-Fe1	117.23(18)
C8-N1-Fe1	115.26(16)	C2-N2-C16	127.9(2)
C2-N2-Fe1	116.94(17)	C16-N2-Fe1	115.12(16)
C5-N3-C17	121.2(2)	C5-N3-Fe1	123.62(17)
C17-N3-Fe1	112.91(16)	C3-N4-C9	121.7(2)

C3-N4-Fe1	123.92(18)	C9-N4-Fe1	112.72(16)
C14-O6-C15	115.8(2)	C22-O8-C23	115.6(2)
C30-P1-C36	109.19(13)	C30-P1-C42	110.89(13)
C36-P1-C42	108.40(13)	C30-P1-C24	105.99(12)
C36-P1-C24	111.99(13)	C42-P1-C24	110.38(13)
N5-C48-C49	170.(2)	N5A-C48A-C49A	177.1(16)

Table A.6 Anisotropic atomic displacement parameters ($\text{\AA}^2$) for **2**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe1	0.0210(2)	0.00811(19)	0.01018(18)	0.00031(15)	0.00234(15)	0.00012(16)
C1	0.0119(12)	0.0117(14)	0.0114(12)	0.0012(10)	0.0013(10)	0.0005(10)
C2	0.0115(12)	0.0111(13)	0.0114(12)	0.0012(10)	0.0033(10)	0.0009(10)
C3	0.0248(15)	0.0125(14)	0.0132(13)	0.0013(11)	0.0028(11)	0.0000(12)
C4	0.0206(13)	0.0119(13)	0.0115(12)	0.0005(11)	0.0022(11)	0.0007(11)
C5	0.0163(13)	0.0120(14)	0.0116(12)	-0.0021(10)	0.0012(10)	-0.0017(11)
C6	0.0231(15)	0.0217(15)	0.0138(13)	0.0018(12)	-0.0018(11)	0.0016(13)
C7	0.0346(17)	0.0154(14)	0.0131(13)	-0.0002(11)	0.0066(12)	-0.0015(13)
C8	0.0137(12)	0.0106(13)	0.0135(13)	0.0030(10)	-0.0012(10)	-0.0005(10)
C9	0.0152(13)	0.0085(13)	0.0132(13)	-0.0006(10)	-0.0008(10)	-0.0001(10)
C10	0.0193(14)	0.0166(14)	0.0120(13)	0.0020(11)	0.0016(11)	-0.0017(12)
C11	0.0179(14)	0.0096(13)	0.0226(15)	0.0046(11)	0.0004(12)	-0.0010(11)
C12	0.0150(13)	0.0111(14)	0.0156(13)	-0.0007(10)	-0.0022(11)	-0.0005(11)
C13	0.0149(13)	0.0143(14)	0.0126(13)	0.0018(10)	-0.0002(11)	-0.0011(11)
C14	0.0192(14)	0.0157(15)	0.0194(14)	-0.0002(11)	0.0003(12)	-0.0005(12)
C15	0.059(2)	0.0172(16)	0.0228(16)	-0.0092(13)	0.0036(16)	-0.0064(16)
C16	0.0128(12)	0.0073(13)	0.0151(13)	0.0003(10)	-0.0002(10)	0.0011(10)
C17	0.0150(13)	0.0108(13)	0.0130(13)	0.0015(10)	0.0001(10)	0.0012(11)
C18	0.0206(14)	0.0136(14)	0.0137(13)	-0.0004(11)	0.0038(11)	0.0025(11)
C19	0.0247(15)	0.0078(13)	0.0199(14)	-0.0039(11)	0.0036(12)	0.0020(11)
C20	0.0152(13)	0.0103(13)	0.0172(13)	0.0024(10)	0.0013(11)	0.0023(11)
C21	0.0133(12)	0.0136(14)	0.0122(13)	0.0003(10)	0.0012(10)	0.0003(11)
C22	0.0157(13)	0.0107(14)	0.0193(14)	0.0020(11)	0.0010(11)	0.0015(11)
C23	0.0336(17)	0.0159(15)	0.0211(15)	0.0102(12)	-0.0016(13)	-0.0009(13)
C24	0.0157(13)	0.0141(14)	0.0168(13)	0.0027(11)	-0.0001(11)	-0.0023(11)
C25	0.0199(14)	0.0160(15)	0.0192(14)	0.0035(11)	0.0007(12)	-0.0004(12)
C26	0.0182(14)	0.0209(16)	0.0229(15)	0.0072(12)	-0.0047(12)	-0.0027(12)
C27	0.0234(15)	0.0278(17)	0.0178(15)	0.0060(13)	-0.0038(12)	-0.0108(13)
C28	0.0256(15)	0.0250(17)	0.0207(15)	-0.0051(13)	0.0056(13)	-0.0070(13)
C29	0.0154(13)	0.0215(16)	0.0235(15)	-0.0035(12)	0.0027(12)	-0.0024(12)
C30	0.0157(13)	0.0127(14)	0.0184(14)	-0.0037(11)	-0.0016(11)	-0.0006(11)

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C31	0.0177(13)	0.0128(14)	0.0162(13)	-0.0031(11)	-0.0033(11)	-0.0017(11)
C32	0.0166(13)	0.0153(15)	0.0215(14)	-0.0045(11)	-0.0038(12)	0.0015(11)
C33	0.0151(13)	0.0187(15)	0.0230(15)	-0.0077(12)	0.0016(12)	-0.0032(11)
C34	0.0230(15)	0.0194(15)	0.0188(14)	0.0004(12)	0.0017(12)	-0.0034(12)
C35	0.0192(14)	0.0155(15)	0.0207(15)	0.0006(11)	-0.0032(12)	0.0018(12)
C36	0.0127(13)	0.0196(15)	0.0238(15)	0.0067(12)	0.0011(11)	0.0035(11)
C37	0.0206(15)	0.0249(17)	0.0346(18)	0.0084(14)	-0.0052(13)	0.0004(13)
C38	0.0261(17)	0.0256(18)	0.051(2)	0.0180(16)	-0.0003(16)	0.0000(14)
C39	0.0240(16)	0.046(2)	0.039(2)	0.0251(17)	0.0099(15)	0.0096(16)
C40	0.0275(17)	0.051(2)	0.0213(16)	0.0092(15)	0.0046(14)	0.0163(16)
C41	0.0224(15)	0.0298(18)	0.0208(15)	0.0041(13)	0.0024(12)	0.0061(13)
C42	0.0192(14)	0.0161(15)	0.0137(13)	-0.0016(11)	-0.0046(11)	0.0025(11)
C43	0.0137(13)	0.0195(15)	0.0228(14)	-0.0007(12)	-0.0035(11)	0.0014(12)
C44	0.0219(15)	0.0168(16)	0.0287(16)	-0.0015(12)	-0.0073(13)	0.0003(12)
C45	0.0295(16)	0.0197(16)	0.0224(15)	-0.0072(12)	-0.0058(13)	0.0072(13)
C46	0.0242(16)	0.0266(17)	0.0200(15)	-0.0029(12)	0.0006(13)	0.0067(13)
C47	0.0201(14)	0.0205(15)	0.0171(14)	0.0002(12)	-0.0010(12)	0.0002(12)
N1	0.0173(11)	0.0092(11)	0.0111(11)	0.0008(8)	0.0014(9)	0.0007(9)
N2	0.0170(11)	0.0074(11)	0.0120(11)	-0.0004(8)	0.0011(9)	-0.0001(9)
N3	0.0178(11)	0.0070(11)	0.0122(11)	0.0008(8)	0.0014(9)	0.0005(9)
N4	0.0185(11)	0.0096(11)	0.0115(11)	0.0008(9)	0.0005(9)	-0.0007(9)
O1	0.0248(10)	0.0114(10)	0.0122(9)	-0.0012(7)	-0.0004(8)	-0.0032(8)
O2	0.0209(10)	0.0102(9)	0.0115(9)	0.0013(7)	0.0011(8)	0.0012(8)
O3	0.0573(15)	0.0190(12)	0.0217(11)	-0.0036(9)	0.0201(11)	-0.0148(11)
O4	0.0333(12)	0.0158(11)	0.0216(11)	0.0008(8)	0.0131(9)	0.0062(9)
O5	0.0434(13)	0.0081(10)	0.0272(11)	-0.0005(8)	0.0066(10)	-0.0026(9)
O6	0.0458(13)	0.0121(10)	0.0171(10)	-0.0047(8)	0.0006(9)	-0.0036(9)
O7	0.0344(12)	0.0091(10)	0.0249(11)	0.0008(8)	0.0058(9)	0.0031(9)
O8	0.0284(11)	0.0120(10)	0.0172(10)	0.0050(8)	0.0005(8)	0.0007(8)
O9	0.0194(10)	0.0122(10)	0.0130(9)	-0.0004(8)	0.0034(8)	-0.0004(8)
O10	0.0506(18)	0.0377(18)	0.104(3)	-0.0005(17)	0.0100(19)	-0.0061(14)
P1	0.0143(3)	0.0137(4)	0.0164(3)	0.0002(3)	-0.0012(3)	0.0009(3)
N5	0.058(6)	0.095(7)	0.126(9)	-0.033(6)	0.011(6)	0.024(5)
C48	0.053(6)	0.076(6)	0.084(6)	-0.015(5)	0.009(5)	-0.005(5)
C49	0.048(6)	0.113(8)	0.083(8)	-0.041(7)	0.019(7)	-0.027(6)
N5A	0.065(5)	0.090(5)	0.177(9)	0.024(6)	-0.005(6)	0.027(5)
C48A	0.025(4)	0.065(4)	0.095(6)	0.005(4)	0.000(4)	0.003(4)
C49A	0.028(4)	0.067(4)	0.043(5)	0.001(4)	0.005(4)	-0.009(3)

Table A.7 Hydrogen atomic coordinates and isotropic atomic displacement parameters ($\text{\AA}^2$) for **2**.

	x/a	y/b	z/c	U(eq)
H6A	-0.0084	0.7126	0.4031	0.03
H6B	-0.0065	0.7860	0.3996	0.03
H6C	-0.0138	0.7522	0.4727	0.03
H7A	0.1537	0.7428	0.3791	0.031
H7B	0.0980	0.7858	0.3463	0.031
H7C	0.0905	0.7127	0.3436	0.031
H10	0.1018	0.9348	0.5077	0.019
H11	0.1020	1.0212	0.5794	0.02
H13	0.0692	0.9145	0.7468	0.017
H15A	0.1234	1.0932	0.8255	0.05
H15B	0.0764	1.0596	0.8747	0.05
H15C	0.0488	1.1024	0.8118	0.05
H18	0.0778	0.5623	0.5022	0.019
H19	0.0762	0.4752	0.5729	0.021
H21	0.0700	0.5813	0.7466	0.016
H23A	0.0483	0.3890	0.8042	0.036
H23B	0.0728	0.4310	0.8690	0.036
H23C	0.1222	0.4017	0.8193	0.036
H25	0.3758	0.8274	0.9483	0.022
H26	0.4503	0.8573	1.0377	0.025
H27	0.4304	0.9405	1.1086	0.028
H28	0.3368	0.9957	1.0904	0.028
H29	0.2622	0.9679	1.0002	0.024
H31	0.1348	0.9347	0.8554	0.019
H32	0.0381	0.9408	0.9062	0.022
H33	0.0247	0.8920	1.0121	0.023
H34	0.1081	0.8368	1.0691	0.024
H35	0.2050	0.8300	1.0188	0.022
H37	0.2768	1.0056	0.8809	0.032
H38	0.2723	1.0731	0.7855	0.041
H39	0.2503	1.0364	0.6727	0.043
H40	0.2300	0.9325	0.6532	0.04
H41	0.2329	0.8643	0.7480	0.029
H43	0.1848	0.7618	0.8924	0.023
H44	0.2046	0.6629	0.8513	0.027
H45	0.2988	0.6423	0.8000	0.029
H46	0.3715	0.7205	0.7849	0.028
H47	0.3520	0.8202	0.8238	0.023
H1O	-0.0553(14)	0.7251(11)	0.6246(14)	0.022
H2O	-0.0525(14)	0.7827(10)	0.6171(15)	0.022
H3O	0.2167(15)	0.6072(19)	0.479(3)	0.096
H4O	0.2759(17)	0.6132(16)	0.487(3)	0.096

	x/a	y/b	z/c	U(eq)
H49A	0.2296	0.8370	0.3768	0.121
H49B	0.3005	0.8445	0.4103	0.121
H49C	0.2514	0.8028	0.4484	0.121
H49D	0.3012	0.8397	0.4030	0.068
H49E	0.2279	0.8321	0.3784	0.068
H49F	0.2799	0.8290	0.3221	0.068

X-ray Crystallographic Data of $(1^+-(CN)_2)(PPh_4)_2$

Figure A.13 (a) ORTEP image of the X-ray crystal structure of complex $(PPh_4)_2[1^+-(CN)_2]$, with disorder in the TAML ligand. The disorder has been refined to two models over two positions (grey and black solid lines). The hydrogen atoms and PPh_4^+ cations have been omitted for clarity. The ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Fe1-C20 2.011(6), Fe1-C21 1.993(6), C20-N5 1.137(7), C21-N6 1.141(7). (b) ORTEP image of the X-ray crystal structure of complex $(PPh_4)_2[1^+-(CN)_2]$. Atom colours: gray for carbon, blue for nitrogen, red for oxygen, and orange for iron.

Table A.8 Crystal data and structure refinement for $1^+-(CN)_2$.

Identification code	$1^+-(CN)_2$	
Empirical formula	C ₆₉ H ₅₄ Fe N ₆ O ₄ P ₂	
Formula weight	1148.97	
Temperature	160(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 17.9956(3) Å	α = 90°.
	b = 14.2843(2) Å	β = 111.3696(10)°.
	c = 23.6299(3) Å	γ = 90°.

Volume	5656.57(15) Å ³
Z	4
Density (calculated)	1.349 Mg/m ³
Absorption coefficient	3.129 mm ⁻¹
F(000)	2392
Crystal size	0.200 x 0.160 x 0.140 mm ³
Theta range for data collection	2.637 to 66.672°.
Index ranges	-21<=h<=20, -16<=k<=16, -27<=l<=28
Reflections collected	34162
Independent reflections	9856 [R(int) = 0.0514]
Completeness to theta = 66.672°	98.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9856 / 1752 / 969
Goodness-of-fit on F ²	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0852, wR2 = 0.2194
R indices (all data)	R1 = 0.1020, wR2 = 0.2320
Extinction coefficient	n/a
Largest diff. peak and hole	1.640 and -0.489 e.Å ⁻³

Table A.9 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1⁺-(CN)₂**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe(1)	7588(1)	7369(1)	1337(1)	38(1)
C(1)	7005(6)	5723(7)	1459(5)	36(2)
C(2)	7873(7)	5738(8)	1897(5)	41(2)
C(3)	6988(7)	8991(6)	541(4)	43(2)
C(4)	8528(7)	8960(9)	1282(6)	61(2)
C(5)	7770(8)	9473(7)	899(4)	54(2)
C(6)	7595(8)	9937(10)	1435(5)	66(2)

Appendix

C(7)	7948(9)	10286(9)	581(6)	76(3)
C(8)	6084(8)	6753(9)	658(7)	38(2)
C(9)	5421(7)	6179(8)	419(6)	43(2)
C(10)	4778(6)	6487(8)	-89(5)	47(2)
C(11)	4792(6)	7364(9)	-328(5)	44(2)
C(12)	5436(6)	7969(8)	-77(5)	41(2)
C(13)	6097(6)	7657(9)	418(6)	38(2)
C(14)	9004(6)	6861(8)	2199(5)	49(2)
C(15)	9610(6)	6341(8)	2614(6)	67(2)
C(16)	10340(7)	6748(10)	2924(7)	77(3)
C(17)	10491(7)	7645(9)	2747(7)	80(3)
C(18)	9913(6)	8160(8)	2313(6)	64(2)
C(19)	9166(5)	7763(7)	2027(5)	49(2)
O(1)	6601(6)	5009(7)	1389(5)	50(2)
O(2)	8174(6)	5045(6)	2210(5)	65(2)
O(3)	6560(6)	9435(6)	102(4)	66(2)
O(4)	9141(6)	9084(8)	1119(5)	84(2)
N(1)	6774(7)	6542(9)	1159(7)	35(2)
N(2)	8227(5)	6572(7)	1897(5)	39(2)
N(3)	6820(6)	8150(8)	721(6)	36(2)
N(4)	8495(5)	8184(6)	1583(4)	42(2)
C(1A)	6762(7)	5658(8)	1327(6)	35(2)
C(2A)	7600(7)	5533(8)	1799(6)	36(2)
C(3A)	7334(8)	8863(8)	511(5)	47(2)
C(5A)	8790(8)	8491(10)	1287(6)	56(2)
C(4A)	8160(8)	9220(8)	910(5)	49(2)
C(6A)	8033(10)	9762(11)	1427(6)	66(2)
C(7A)	8485(11)	9809(11)	559(7)	76(3)
C(8A)	6065(9)	6882(11)	578(8)	38(2)
C(9A)	5347(8)	6405(10)	270(6)	43(2)
C(10A)	4779(7)	6831(11)	-228(6)	45(2)
C(11A)	4938(8)	7702(10)	-413(6)	45(2)
C(12A)	5659(7)	8169(9)	-119(6)	41(2)
C(13A)	6246(8)	7755(10)	374(7)	38(2)
C(14A)	8869(3)	6433(6)	2171(4)	43(2)

C(15A)	9371(4)	5834(5)	2607(4)	52(2)
C(16A)	10160(4)	6087(6)	2925(4)	62(2)
C(17A)	10447(4)	6939(7)	2806(4)	64(3)
C(18A)	9945(5)	7538(6)	2370(4)	57(2)
C(19A)	9156(4)	7286(6)	2053(4)	46(2)
O(1A)	6277(6)	5019(8)	1223(5)	42(2)
O(2A)	7809(6)	4802(6)	2095(4)	50(2)
O(3A)	7049(8)	9156(8)	-8(4)	80(3)
O(4A)	9508(7)	8499(10)	1286(6)	89(3)
N(1A)	6689(9)	6517(10)	1067(9)	36(2)
N(2A)	8076(6)	6293(8)	1840(5)	35(2)
N(3A)	7012(7)	8135(9)	708(7)	37(2)
N(4A)	8607(5)	7876(8)	1625(5)	45(2)
C(20)	7275(3)	7944(4)	1995(2)	49(1)
C(21)	7931(3)	6745(4)	719(2)	45(1)
N(5)	7123(3)	8256(5)	2382(2)	70(2)
N(6)	8144(3)	6344(4)	388(2)	55(1)
C(22)	6007(3)	511(3)	3433(2)	37(1)
C(23)	6044(4)	-347(4)	3159(3)	49(1)
C(24)	6295(4)	-1137(4)	3507(3)	54(1)
C(25)	6507(3)	-1082(4)	4131(3)	50(1)
C(26)	6475(3)	-232(4)	4403(3)	48(1)
C(27)	6222(3)	562(4)	4057(2)	41(1)
C(28)	6341(3)	1847(4)	2598(2)	43(1)
C(29)	6967(4)	1290(5)	2628(3)	70(2)
C(30)	7501(5)	1608(6)	2363(4)	99(3)
C(31)	7372(5)	2427(6)	2056(4)	99(3)
C(32)	6769(4)	2995(5)	2038(3)	67(2)
C(33)	6252(3)	2719(4)	2321(2)	45(1)
C(34)	5554(3)	2505(3)	3386(2)	36(1)
C(35)	4808(3)	2819(3)	3355(2)	38(1)
C(36)	4751(3)	3588(4)	3698(3)	48(1)
C(37)	5432(4)	4042(4)	4061(3)	53(1)
C(38)	6169(4)	3741(4)	4090(3)	55(2)
C(39)	6237(3)	2977(4)	3754(3)	49(1)

C(40)	4704(3)	1193(3)	2387(2)	35(1)
C(41)	4165(3)	697(3)	2572(3)	45(1)
C(42)	3444(3)	441(4)	2147(3)	54(1)
C(43)	3253(4)	669(4)	1547(3)	55(2)
C(44)	3774(3)	1171(4)	1364(3)	52(1)
C(45)	4506(3)	1442(3)	1783(2)	41(1)
C(46)	1003(3)	8132(3)	663(3)	40(1)
C(47)	1364(3)	8104(4)	1287(3)	51(1)
C(48)	1520(4)	8920(4)	1623(3)	61(2)
C(49)	1325(3)	9761(4)	1328(4)	63(2)
C(50)	985(3)	9801(4)	711(4)	63(2)
C(51)	815(3)	8997(3)	369(3)	48(1)
C(52)	-223(3)	7271(3)	-364(2)	43(1)
C(53)	-352(4)	7263(5)	-974(3)	71(2)
C(54)	-1093(5)	7472(5)	-1405(3)	79(2)
C(55)	-1722(4)	7649(4)	-1241(3)	57(2)
C(56)	-1621(4)	7728(5)	-639(3)	66(2)
C(57)	-872(4)	7541(5)	-202(3)	67(2)
C(58)	1436(3)	6830(3)	-152(3)	45(1)
C(59)	2035(4)	7449(4)	-114(3)	56(2)
C(60)	2553(4)	7247(5)	-410(3)	66(2)
C(61)	2471(4)	6449(4)	-738(3)	59(2)
C(62)	1876(5)	5838(4)	-775(4)	83(2)
C(63)	1374(5)	6014(4)	-459(4)	82(2)
C(64)	762(3)	6140(3)	729(2)	40(1)
C(65)	205(5)	6099(5)	998(4)	85(3)
C(66)	285(5)	5475(5)	1456(4)	79(2)
C(67)	919(4)	4875(4)	1651(3)	56(2)
C(68)	1471(4)	4890(5)	1381(4)	80(2)
C(69)	1404(4)	5523(4)	928(4)	67(2)
P(1)	5652(1)	1513(1)	2954(1)	33(1)
P(2)	737(1)	7078(1)	214(1)	38(1)

Table A.10 Atomic Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\mathbf{1^+-(CN)_2}$

Fe(1)-N(2)	1.807(9)
Fe(1)-N(1)	1.807(11)
Fe(1)-N(3A)	1.832(11)
Fe(1)-N(4A)	1.856(9)
Fe(1)-N(4)	1.916(8)
Fe(1)-N(1A)	1.938(12)
Fe(1)-N(2A)	1.946(10)
Fe(1)-N(3)	1.950(9)
Fe(1)-C(21)	1.993(6)
Fe(1)-C(20)	2.011(6)
C(1)-O(1)	1.227(11)
C(1)-N(1)	1.353(10)
C(1)-C(2)	1.528(13)
C(2)-O(2)	1.236(10)
C(2)-N(2)	1.350(12)
C(3)-O(3)	1.219(10)
C(3)-N(3)	1.346(11)
C(3)-C(5)	1.517(13)
C(4)-O(4)	1.306(13)
C(4)-N(4)	1.329(13)
C(4)-C(5)	1.522(16)
C(5)-C(7)	1.480(13)
C(5)-C(6)	1.561(15)
C(8)-C(9)	1.388(11)
C(8)-N(1)	1.400(10)
C(8)-C(13)	1.414(11)
C(9)-C(10)	1.399(13)
C(10)-C(11)	1.378(14)
C(11)-C(12)	1.392(14)
C(12)-C(13)	1.403(11)
C(13)-N(3)	1.422(11)
C(14)-N(2)	1.382(11)
C(14)-C(15)	1.387(12)
C(14)-C(19)	1.414(12)

C(15)-C(16)	1.377(13)
C(16)-C(17)	1.405(14)
C(17)-C(18)	1.378(13)
C(18)-C(19)	1.386(12)
C(19)-N(4)	1.413(11)
C(1A)-O(1A)	1.225(12)
C(1A)-N(1A)	1.357(12)
C(1A)-C(2A)	1.525(14)
C(2A)-O(2A)	1.237(11)
C(2A)-N(2A)	1.364(13)
C(3A)-O(3A)	1.219(12)
C(3A)-N(3A)	1.353(12)
C(3A)-C(4A)	1.528(15)
C(5A)-O(4A)	1.294(14)
C(5A)-N(4A)	1.308(14)
C(5A)-C(4A)	1.558(17)
C(4A)-C(7A)	1.445(14)
C(4A)-C(6A)	1.533(16)
C(8A)-N(1A)	1.387(11)
C(8A)-C(9A)	1.407(12)
C(8A)-C(13A)	1.417(13)
C(9A)-C(10A)	1.385(15)
C(10A)-C(11A)	1.382(16)
C(11A)-C(12A)	1.398(15)
C(12A)-C(13A)	1.387(12)
C(13A)-N(3A)	1.423(12)
C(14A)-N(2A)	1.370(10)
C(14A)-C(15A)	1.3900
C(14A)-C(19A)	1.3900
C(15A)-C(16A)	1.3900
C(16A)-C(17A)	1.3900
C(17A)-C(18A)	1.3900
C(18A)-C(19A)	1.3900
C(19A)-N(4A)	1.407(11)
C(20)-N(5)	1.137(7)

C(21)-N(6)	1.141(7)
C(22)-C(27)	1.384(7)
C(22)-C(23)	1.399(7)
C(22)-P(1)	1.792(5)
C(23)-C(24)	1.373(7)
C(24)-C(25)	1.384(8)
C(25)-C(26)	1.385(8)
C(26)-C(27)	1.376(7)
C(28)-C(29)	1.360(8)
C(28)-C(33)	1.389(7)
C(28)-P(1)	1.798(5)
C(29)-C(30)	1.403(9)
C(30)-C(31)	1.351(10)
C(31)-C(32)	1.343(10)
C(32)-C(33)	1.385(8)
C(34)-C(35)	1.393(7)
C(34)-C(39)	1.394(7)
C(34)-P(1)	1.791(5)
C(35)-C(36)	1.391(7)
C(36)-C(37)	1.375(8)
C(37)-C(38)	1.372(9)
C(38)-C(39)	1.380(8)
C(40)-C(45)	1.386(7)
C(40)-C(41)	1.393(7)
C(40)-P(1)	1.802(5)
C(41)-C(42)	1.370(8)
C(42)-C(43)	1.371(9)
C(43)-C(44)	1.370(8)
C(44)-C(45)	1.384(8)
C(46)-C(47)	1.380(8)
C(46)-C(51)	1.397(7)
C(46)-P(2)	1.802(5)
C(47)-C(48)	1.380(8)
C(48)-C(49)	1.368(9)
C(49)-C(50)	1.360(10)

C(50)-C(51)	1.375(8)
C(52)-C(53)	1.375(9)
C(52)-C(57)	1.410(9)
C(52)-P(2)	1.790(6)
C(53)-C(54)	1.384(10)
C(54)-C(55)	1.349(10)
C(55)-C(56)	1.370(9)
C(56)-C(57)	1.393(9)
C(58)-C(63)	1.356(8)
C(58)-C(59)	1.371(7)
C(58)-P(2)	1.805(5)
C(59)-C(60)	1.385(8)
C(60)-C(61)	1.356(9)
C(61)-C(62)	1.359(10)
C(62)-C(63)	1.390(9)
C(64)-C(65)	1.370(8)
C(64)-C(69)	1.392(8)
C(64)-P(2)	1.798(5)
C(65)-C(66)	1.367(9)
C(66)-C(67)	1.366(9)
C(67)-C(68)	1.362(10)
C(68)-C(69)	1.373(9)

N(2)-Fe(1)-N(1)	90.2(4)
N(3A)-Fe(1)-N(4A)	104.9(4)
N(2)-Fe(1)-N(4)	85.2(4)
N(1)-Fe(1)-N(4)	175.3(4)
N(3A)-Fe(1)-N(1A)	87.1(4)
N(4A)-Fe(1)-N(1A)	164.0(7)
N(3A)-Fe(1)-N(2A)	164.4(6)
N(4A)-Fe(1)-N(2A)	85.3(4)
N(1A)-Fe(1)-N(2A)	80.9(4)
N(2)-Fe(1)-N(3)	174.8(4)
N(1)-Fe(1)-N(3)	84.6(4)
N(4)-Fe(1)-N(3)	100.0(4)

N(2)-Fe(1)-C(21)	88.3(4)
N(1)-Fe(1)-C(21)	88.7(7)
N(3A)-Fe(1)-C(21)	84.7(6)
N(4A)-Fe(1)-C(21)	85.1(4)
N(4)-Fe(1)-C(21)	92.1(4)
N(1A)-Fe(1)-C(21)	85.5(8)
N(2A)-Fe(1)-C(21)	84.4(4)
N(3)-Fe(1)-C(21)	91.9(5)
N(2)-Fe(1)-C(20)	88.5(4)
N(1)-Fe(1)-C(20)	90.9(7)
N(3A)-Fe(1)-C(20)	98.6(6)
N(4A)-Fe(1)-C(20)	94.3(5)
N(4)-Fe(1)-C(20)	88.0(4)
N(1A)-Fe(1)-C(20)	94.4(8)
N(2A)-Fe(1)-C(20)	92.4(4)
N(3)-Fe(1)-C(20)	91.3(5)
C(21)-Fe(1)-C(20)	176.7(2)
O(1)-C(1)-N(1)	126.5(10)
O(1)-C(1)-C(2)	120.8(9)
N(1)-C(1)-C(2)	112.6(8)
O(2)-C(2)-N(2)	127.0(10)
O(2)-C(2)-C(1)	120.7(10)
N(2)-C(2)-C(1)	112.3(7)
O(3)-C(3)-N(3)	126.0(10)
O(3)-C(3)-C(5)	114.1(8)
N(3)-C(3)-C(5)	119.9(8)
O(4)-C(4)-N(4)	118.5(12)
O(4)-C(4)-C(5)	115.4(10)
N(4)-C(4)-C(5)	121.0(9)
C(7)-C(5)-C(3)	113.7(9)
C(7)-C(5)-C(4)	111.5(11)
C(3)-C(5)-C(4)	124.1(9)
C(7)-C(5)-C(6)	102.9(10)
C(3)-C(5)-C(6)	103.0(10)
C(4)-C(5)-C(6)	97.1(9)

C(9)-C(8)-N(1)	125.7(9)
C(9)-C(8)-C(13)	120.8(9)
N(1)-C(8)-C(13)	113.4(9)
C(8)-C(9)-C(10)	118.9(10)
C(11)-C(10)-C(9)	120.2(9)
C(10)-C(11)-C(12)	121.8(9)
C(11)-C(12)-C(13)	118.6(10)
C(12)-C(13)-C(8)	119.5(9)
C(12)-C(13)-N(3)	127.3(9)
C(8)-C(13)-N(3)	113.3(8)
N(2)-C(14)-C(15)	126.3(10)
N(2)-C(14)-C(19)	113.6(8)
C(15)-C(14)-C(19)	120.0(9)
C(16)-C(15)-C(14)	120.2(11)
C(15)-C(16)-C(17)	118.5(11)
C(18)-C(17)-C(16)	122.2(11)
C(17)-C(18)-C(19)	118.6(10)
C(18)-C(19)-N(4)	127.0(9)
C(18)-C(19)-C(14)	119.8(9)
N(4)-C(19)-C(14)	113.1(8)
C(1)-N(1)-C(8)	129.5(10)
C(1)-N(1)-Fe(1)	112.1(7)
C(8)-N(1)-Fe(1)	116.7(7)
C(2)-N(2)-C(14)	130.7(9)
C(2)-N(2)-Fe(1)	112.4(6)
C(14)-N(2)-Fe(1)	116.4(7)
C(3)-N(3)-C(13)	123.5(8)
C(3)-N(3)-Fe(1)	124.5(7)
C(13)-N(3)-Fe(1)	111.2(6)
C(4)-N(4)-C(19)	124.0(8)
C(4)-N(4)-Fe(1)	122.9(7)
C(19)-N(4)-Fe(1)	111.7(6)
O(1A)-C(1A)-N(1A)	129.7(11)
O(1A)-C(1A)-C(2A)	120.1(10)
N(1A)-C(1A)-C(2A)	110.1(9)

O(2A)-C(2A)-N(2A)	125.4(11)
O(2A)-C(2A)-C(1A)	121.9(11)
N(2A)-C(2A)-C(1A)	112.7(8)
O(3A)-C(3A)-N(3A)	122.3(11)
O(3A)-C(3A)-C(4A)	117.6(10)
N(3A)-C(3A)-C(4A)	119.2(9)
O(4A)-C(5A)-N(4A)	118.7(13)
O(4A)-C(5A)-C(4A)	120.8(11)
N(4A)-C(5A)-C(4A)	120.4(11)
C(7A)-C(4A)-C(3A)	110.3(10)
C(7A)-C(4A)-C(6A)	111.8(11)
C(3A)-C(4A)-C(6A)	105.3(12)
C(7A)-C(4A)-C(5A)	110.8(12)
C(3A)-C(4A)-C(5A)	118.1(9)
C(6A)-C(4A)-C(5A)	99.8(10)
N(1A)-C(8A)-C(9A)	124.2(11)
N(1A)-C(8A)-C(13A)	113.4(10)
C(9A)-C(8A)-C(13A)	122.1(10)
C(10A)-C(9A)-C(8A)	118.8(12)
C(11A)-C(10A)-C(9A)	119.3(11)
C(10A)-C(11A)-C(12A)	122.2(11)
C(13A)-C(12A)-C(11A)	119.9(11)
C(12A)-C(13A)-C(8A)	117.5(10)
C(12A)-C(13A)-N(3A)	126.2(10)
C(8A)-C(13A)-N(3A)	116.3(9)
N(2A)-C(14A)-C(15A)	126.5(7)
N(2A)-C(14A)-C(19A)	113.5(7)
C(15A)-C(14A)-C(19A)	120.0
C(16A)-C(15A)-C(14A)	120.0
C(15A)-C(16A)-C(17A)	120.0
C(18A)-C(17A)-C(16A)	120.0
C(19A)-C(18A)-C(17A)	120.0
C(18A)-C(19A)-C(14A)	120.0
C(18A)-C(19A)-N(4A)	122.9(6)
C(14A)-C(19A)-N(4A)	117.0(6)

C(1A)-N(1A)-C(8A)	129.3(11)
C(1A)-N(1A)-Fe(1)	119.2(8)
C(8A)-N(1A)-Fe(1)	111.3(8)
C(2A)-N(2A)-C(14A)	130.8(9)
C(2A)-N(2A)-Fe(1)	117.0(7)
C(14A)-N(2A)-Fe(1)	112.2(7)
C(3A)-N(3A)-C(13A)	123.5(10)
C(3A)-N(3A)-Fe(1)	123.4(8)
C(13A)-N(3A)-Fe(1)	111.7(7)
C(5A)-N(4A)-C(19A)	125.1(10)
C(5A)-N(4A)-Fe(1)	118.2(9)
C(19A)-N(4A)-Fe(1)	111.8(7)
N(5)-C(20)-Fe(1)	177.5(5)
N(6)-C(21)-Fe(1)	175.9(5)
C(27)-C(22)-C(23)	119.8(5)
C(27)-C(22)-P(1)	121.9(4)
C(23)-C(22)-P(1)	118.3(4)
C(24)-C(23)-C(22)	120.2(5)
C(23)-C(24)-C(25)	119.6(5)
C(24)-C(25)-C(26)	120.2(5)
C(27)-C(26)-C(25)	120.5(5)
C(26)-C(27)-C(22)	119.6(5)
C(29)-C(28)-C(33)	120.0(5)
C(29)-C(28)-P(1)	121.3(4)
C(33)-C(28)-P(1)	118.6(4)
C(28)-C(29)-C(30)	118.5(6)
C(31)-C(30)-C(29)	120.5(6)
C(32)-C(31)-C(30)	121.3(6)
C(31)-C(32)-C(33)	119.3(6)
C(32)-C(33)-C(28)	120.1(6)
C(35)-C(34)-C(39)	119.3(5)
C(35)-C(34)-P(1)	121.2(4)
C(39)-C(34)-P(1)	119.5(4)
C(36)-C(35)-C(34)	119.9(5)
C(37)-C(36)-C(35)	119.9(5)

C(38)-C(37)-C(36)	120.6(5)
C(37)-C(38)-C(39)	120.3(5)
C(38)-C(39)-C(34)	120.0(5)
C(45)-C(40)-C(41)	120.4(5)
C(45)-C(40)-P(1)	121.2(4)
C(41)-C(40)-P(1)	118.3(4)
C(42)-C(41)-C(40)	119.2(5)
C(41)-C(42)-C(43)	120.5(5)
C(44)-C(43)-C(42)	120.5(5)
C(43)-C(44)-C(45)	120.2(5)
C(44)-C(45)-C(40)	119.1(5)
C(47)-C(46)-C(51)	119.5(5)
C(47)-C(46)-P(2)	121.7(4)
C(51)-C(46)-P(2)	118.8(4)
C(46)-C(47)-C(48)	120.5(6)
C(49)-C(48)-C(47)	119.3(6)
C(50)-C(49)-C(48)	120.9(5)
C(49)-C(50)-C(51)	120.8(6)
C(50)-C(51)-C(46)	119.0(6)
C(53)-C(52)-C(57)	116.6(6)
C(53)-C(52)-P(2)	123.2(5)
C(57)-C(52)-P(2)	119.9(4)
C(52)-C(53)-C(54)	121.3(6)
C(55)-C(54)-C(53)	120.9(7)
C(54)-C(55)-C(56)	120.4(6)
C(55)-C(56)-C(57)	118.8(6)
C(56)-C(57)-C(52)	121.6(6)
C(63)-C(58)-C(59)	120.0(5)
C(63)-C(58)-P(2)	119.3(4)
C(59)-C(58)-P(2)	120.7(4)
C(58)-C(59)-C(60)	119.4(6)
C(61)-C(60)-C(59)	120.7(6)
C(60)-C(61)-C(62)	119.8(6)
C(61)-C(62)-C(63)	120.0(7)
C(58)-C(63)-C(62)	120.0(6)

C(65)-C(64)-C(69)	118.3(5)
C(65)-C(64)-P(2)	120.2(4)
C(69)-C(64)-P(2)	120.9(4)
C(66)-C(65)-C(64)	120.8(6)
C(67)-C(66)-C(65)	120.6(6)
C(68)-C(67)-C(66)	119.7(6)
C(67)-C(68)-C(69)	120.2(6)
C(68)-C(69)-C(64)	120.5(6)
C(34)-P(1)-C(22)	111.0(2)
C(34)-P(1)-C(28)	106.5(2)
C(22)-P(1)-C(28)	111.0(2)
C(34)-P(1)-C(40)	111.2(2)
C(22)-P(1)-C(40)	106.9(2)
C(28)-P(1)-C(40)	110.3(2)
C(52)-P(2)-C(64)	114.2(2)
C(52)-P(2)-C(46)	107.2(2)
C(64)-P(2)-C(46)	106.8(2)
C(52)-P(2)-C(58)	108.1(3)
C(64)-P(2)-C(58)	109.1(2)
C(46)-P(2)-C(58)	111.3(2)

Symmetry transformations used to generate equivalent atoms:

Table A.11 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\mathbf{1}^+ \cdot (\text{CN})_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Fe(1)	38(1)	46(1)	30(1)	12(1)	14(1)	7(1)
C(1)	39(3)	39(3)	38(3)	9(3)	24(3)	5(3)
C(2)	38(3)	41(3)	45(3)	12(3)	16(3)	8(3)
C(3)	55(3)	39(3)	31(3)	9(2)	11(3)	-1(3)
C(4)	54(3)	55(4)	71(3)	14(3)	21(3)	-6(3)

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C(5)	63(4)	46(3)	46(3)	4(3)	12(3)	-12(3)
C(6)	71(5)	63(4)	57(3)	-9(3)	15(4)	-9(4)
C(7)	80(6)	72(6)	75(6)	24(5)	27(5)	-15(5)
C(8)	39(3)	40(3)	39(3)	5(3)	19(3)	8(2)
C(9)	42(3)	43(4)	48(4)	6(3)	21(3)	5(3)
C(10)	43(3)	44(4)	52(4)	4(3)	16(3)	1(3)
C(11)	43(3)	40(4)	45(3)	3(3)	11(3)	-1(3)
C(12)	43(3)	39(4)	39(3)	4(3)	12(3)	-1(3)
C(13)	41(3)	40(3)	34(3)	0(2)	14(3)	2(3)
C(14)	38(3)	47(3)	61(3)	8(3)	17(2)	8(3)
C(15)	47(3)	58(3)	81(3)	9(3)	7(3)	8(3)
C(16)	48(3)	70(4)	95(4)	9(4)	4(3)	6(3)
C(17)	49(4)	73(4)	103(5)	7(4)	9(4)	8(3)
C(18)	41(3)	61(4)	87(4)	3(4)	19(3)	3(3)
C(19)	39(3)	49(3)	62(3)	6(3)	21(3)	4(3)
O(1)	49(5)	48(4)	57(5)	13(3)	23(4)	-3(4)
O(2)	54(5)	45(4)	80(5)	31(4)	4(4)	4(3)
O(3)	78(5)	51(4)	51(4)	31(3)	2(4)	5(4)
O(4)	74(4)	91(6)	97(5)	4(5)	43(4)	-18(4)
N(1)	37(3)	40(3)	36(4)	8(3)	23(3)	8(3)
N(2)	36(3)	40(3)	45(3)	8(3)	20(2)	8(2)
N(3)	46(4)	34(3)	26(3)	8(2)	10(3)	5(3)
N(4)	42(3)	48(4)	45(3)	3(3)	26(2)	1(3)
C(1A)	32(4)	40(3)	37(4)	7(3)	18(3)	2(3)
C(2A)	36(3)	37(3)	39(3)	8(3)	19(3)	1(3)
C(3A)	60(4)	45(3)	35(3)	8(3)	14(3)	-5(3)
C(5A)	59(3)	53(4)	58(3)	2(3)	23(3)	-11(3)
C(4A)	60(4)	43(3)	44(3)	-2(3)	20(3)	-11(3)
C(6A)	71(5)	63(4)	57(3)	-9(3)	15(4)	-9(4)
C(7A)	93(7)	72(6)	64(6)	14(5)	30(5)	-14(5)
C(8A)	39(3)	42(3)	37(3)	4(3)	18(3)	9(3)
C(9A)	42(3)	46(4)	44(4)	4(3)	18(3)	5(3)
C(10A)	42(3)	47(4)	46(4)	6(3)	15(3)	5(3)
C(11A)	46(4)	47(4)	43(4)	2(3)	15(3)	6(3)
C(12A)	44(4)	42(4)	36(3)	2(3)	15(3)	7(3)

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C(13A)	43(3)	39(3)	33(3)	1(3)	16(3)	6(3)
C(14A)	34(3)	45(3)	53(3)	4(3)	20(3)	4(3)
C(15A)	36(3)	51(4)	66(4)	8(4)	16(3)	4(3)
C(16A)	41(4)	63(4)	75(4)	6(4)	13(3)	3(3)
C(17A)	39(4)	66(4)	83(4)	11(4)	19(3)	-1(3)
C(18A)	40(3)	59(3)	73(3)	5(3)	21(3)	-1(3)
C(19A)	37(3)	51(3)	57(3)	3(3)	24(2)	1(3)
O(1A)	39(5)	47(4)	42(5)	10(4)	16(4)	-10(4)
O(2A)	45(5)	39(4)	54(5)	14(3)	2(4)	-5(3)
O(3A)	105(7)	79(6)	41(4)	23(4)	7(4)	-17(5)
O(4A)	73(5)	98(7)	98(6)	18(6)	36(5)	-9(5)
N(1A)	36(3)	39(3)	37(4)	7(3)	20(3)	4(3)
N(2A)	31(3)	38(4)	40(3)	9(3)	18(3)	5(3)
N(3A)	45(4)	36(3)	28(3)	2(3)	13(3)	5(3)
N(4A)	43(3)	48(4)	50(3)	1(3)	25(3)	1(3)
C(20)	37(3)	70(4)	35(3)	10(3)	5(2)	15(3)
C(21)	50(3)	48(3)	44(3)	4(2)	27(3)	-13(2)
N(5)	48(3)	115(5)	39(3)	-2(3)	6(2)	30(3)
N(6)	61(3)	59(3)	55(3)	-10(2)	33(3)	-18(2)
C(22)	38(3)	33(2)	47(3)	7(2)	24(2)	1(2)
C(23)	66(4)	38(3)	55(3)	8(2)	38(3)	7(2)
C(24)	73(4)	31(3)	69(4)	9(3)	38(3)	9(3)
C(25)	54(3)	38(3)	62(4)	19(3)	24(3)	5(2)
C(26)	55(3)	43(3)	48(3)	6(2)	22(3)	-6(2)
C(27)	41(3)	37(3)	50(3)	4(2)	22(2)	-3(2)
C(28)	35(3)	46(3)	51(3)	16(2)	21(2)	1(2)
C(29)	64(4)	79(4)	86(5)	49(4)	50(4)	34(3)
C(30)	84(5)	121(7)	130(7)	82(6)	83(5)	56(5)
C(31)	67(5)	130(7)	127(7)	84(6)	68(5)	31(5)
C(32)	72(4)	68(4)	62(4)	29(3)	25(3)	-15(3)
C(33)	51(3)	38(3)	48(3)	6(2)	19(3)	-6(2)
C(34)	40(3)	25(2)	40(3)	3(2)	13(2)	-3(2)
C(35)	43(3)	30(2)	41(3)	-3(2)	14(2)	-6(2)
C(36)	51(3)	40(3)	56(3)	-9(2)	22(3)	0(2)
C(37)	69(4)	36(3)	50(3)	-5(2)	17(3)	-3(3)

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C(38)	60(4)	38(3)	55(3)	-5(2)	6(3)	-17(3)
C(39)	41(3)	40(3)	60(3)	1(2)	13(3)	-9(2)
C(40)	36(2)	23(2)	47(3)	-1(2)	16(2)	2(2)
C(41)	51(3)	35(3)	57(3)	-12(2)	29(3)	-13(2)
C(42)	52(3)	42(3)	72(4)	-15(3)	27(3)	-18(2)
C(43)	50(3)	43(3)	64(4)	-14(3)	11(3)	-11(2)
C(44)	54(3)	48(3)	48(3)	0(2)	12(3)	1(3)
C(45)	45(3)	30(2)	52(3)	2(2)	22(2)	1(2)
C(46)	24(2)	31(2)	64(3)	-9(2)	19(2)	-5(2)
C(47)	42(3)	39(3)	71(4)	-12(3)	21(3)	-3(2)
C(48)	51(3)	43(3)	81(4)	-20(3)	17(3)	-11(3)
C(49)	42(3)	40(3)	102(5)	-29(3)	20(3)	-12(2)
C(50)	43(3)	26(3)	113(6)	-1(3)	21(3)	-2(2)
C(51)	31(2)	31(3)	78(4)	0(2)	16(3)	1(2)
C(52)	54(3)	27(2)	54(3)	-5(2)	25(3)	-16(2)
C(53)	72(4)	83(5)	65(4)	-18(4)	32(4)	19(4)
C(54)	93(6)	88(5)	46(4)	-17(3)	12(4)	31(4)
C(55)	58(4)	47(3)	53(3)	-8(3)	6(3)	-17(3)
C(56)	40(3)	92(5)	67(4)	22(4)	19(3)	-7(3)
C(57)	48(3)	103(5)	52(3)	22(3)	22(3)	-7(3)
C(58)	50(3)	28(2)	72(4)	2(2)	39(3)	3(2)
C(59)	71(4)	39(3)	75(4)	3(3)	49(3)	-7(3)
C(60)	74(4)	61(4)	86(5)	7(3)	58(4)	-10(3)
C(61)	69(4)	56(4)	71(4)	28(3)	49(3)	26(3)
C(62)	108(6)	38(3)	145(7)	-3(4)	97(6)	11(3)
C(63)	99(5)	35(3)	153(7)	-16(4)	96(6)	-11(3)
C(64)	44(3)	19(2)	58(3)	-6(2)	22(2)	-3(2)
C(65)	100(6)	76(5)	114(6)	50(4)	83(5)	55(4)
C(66)	114(6)	58(4)	101(5)	28(4)	81(5)	36(4)
C(67)	68(4)	30(3)	65(4)	5(3)	19(3)	-9(3)
C(68)	51(4)	51(4)	135(7)	46(4)	32(4)	5(3)
C(69)	41(3)	50(3)	120(6)	21(4)	43(4)	3(3)
P(1)	34(1)	27(1)	43(1)	4(1)	18(1)	-2(1)
P(2)	39(1)	24(1)	56(1)	-5(1)	26(1)	-4(1)

Table A.12 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\mathbf{1}^+(\text{CN})_2$.

	x	y	z	U(eq)
H(6A)	8034	10361	1656	99
H(6B)	7547	9450	1712	99
H(6C)	7096	10292	1275	99
H(7A)	7988	10078	198	114
H(7B)	8455	10568	839	114
H(7C)	7520	10749	497	114
H(9)	5403	5587	596	52
H(10)	4330	6089	-269	56
H(11)	4351	7561	-673	52
H(12)	5427	8580	-238	49
H(15)	9521	5704	2686	80
H(16)	10732	6429	3250	93
H(17)	11010	7904	2933	96
H(18)	10024	8775	2212	77
H(6A1)	7770	10359	1272	99
H(6A2)	8550	9880	1750	99
H(6A3)	7697	9392	1589	99
H(7A1)	8620	9424	267	114
H(7A2)	8966	10122	833	114
H(7A3)	8088	10280	340	114
H(9A)	5253	5803	400	52
H(10A)	4286	6528	-439	54
H(11A)	4543	7993	-751	55
H(12A)	5747	8769	-257	49
H(15A)	9175	5252	2688	62
H(16A)	10503	5677	3223	75
H(17A)	10986	7112	3023	76

H(18A)	10141	8121	2290	69
H(23)	5895	-383	2730	58
H(24)	6323	-1719	3321	65
H(25)	6674	-1629	4373	61
H(26)	6630	-197	4833	58
H(27)	6195	1142	4245	49
H(29)	7040	698	2825	84
H(30)	7959	1244	2399	119
H(31)	7714	2605	1849	119
H(32)	6697	3580	1834	80
H(33)	5836	3126	2325	54
H(35)	4338	2508	3100	46
H(36)	4243	3800	3681	58
H(37)	5391	4569	4293	64
H(38)	6635	4059	4343	66
H(39)	6748	2773	3775	58
H(41)	4296	539	2987	54
H(42)	3073	102	2269	65
H(43)	2755	477	1255	66
H(44)	3633	1333	948	62
H(45)	4868	1794	1659	50
H(47)	1505	7518	1488	61
H(48)	1761	8899	2053	73
H(49)	1429	10325	1557	76
H(50)	864	10393	515	75
H(51)	574	9028	-61	57
H(53)	76	7111	-1103	85
H(54)	-1160	7490	-1823	95
H(55)	-2239	7720	-1544	68
H(56)	-2053	7907	-523	80
H(57)	-797	7596	216	80
H(59)	2093	8011	113	67
H(60)	2971	7672	-382	79
H(61)	2828	6317	-940	70
H(62)	1804	5290	-1018	99

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H(63)	986	5563	-458	98
H(65)	-242	6508	865	102
H(66)	-104	5459	1640	95
H(67)	975	4450	1973	67
H(68)	1904	4461	1507	96
H(69)	1798	5540	748	81