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Review article

Visible light generation of high-valent metal-oxo intermediates and mechanistic insights into catalytic oxidations



Inorganic Biochemistry

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ARTICLE INFO ABSTRACT Keywords: High-valent metal-oxo complexes play central roles as active oxygen atom transfer (OAT) agents in many en-Metal-oxo species zymatic and synthetic oxidation catalysis. This review focuses on our recent advances in application of photo-Porphyrin chemical approaches to probe the oxidizing metal-oxo species with different metals and macrocyclic ligands. Corrole Under visible light irradiation, a variety of important metal-oxo species including iron-oxo porphyrins, man-Salen ganese-oxo porphyrin/corroles, ruthenium-oxo porphyrins, and chromium-oxo salens have been successfully Photocatalytic oxidation generated. Kinetical studies in real time have provided mechanistic insights as to the reactivity and reaction Visible light pathways of the metal-oxo intermediates in their oxidation reactions. In photo-induced ligand cleavage reactions, metals in n^+ oxidation state with the oxygen-containing ligands bromate, chlorate, or nitrites were photolyzed. Homolytic cleavage of the O-X bond in the ligand gives $(n + 1)^+$ oxidation state metal-oxo species, and heterolytic cleavage gives $(n + 2)^+$ oxidation state metal-oxo species. In photo-disproportionation reac-

tions, reactive M^{n+1} -oxo species can be formed by photolysis of μ -oxo dimeric M^{n+} complexes with the concomitant formation of M^{n-1} products. Importantly, the oxidation of M^{n-1} products by molecular oxygen (O₂) to regenerate the μ -oxo dimeric M^{n+} complexes in photo-disproportionation reactions represents an attractive and green catalytic cycle for the development of photocatalytic aerobic oxidations.

1. Introduction

Catalytic oxidations are core processes in petrochemistry and millions of tons of high-value oxygenated compounds are annually produced and applied to the manufacturing of fine chemicals worldwide [1–3]. In nature, the ubiquitous cytochrome P450 enzymes (P450s) with an iron protoporphyrin IX core catalyze a wide variety of oxidation reactions with exceptionally high reactivity and selectivity [4,5]. Not surprisingly, many transition metal complexes are designed to develop bioinspired oxidation catalysts and to aid in understanding important biological processes [6,7]. As a result, these synthetic catalysts typically consist of transition metals such as iron, manganese, chromium, or ruthenium in a macrocyclic (porphyrin and porphyrinoid) or "clamp"like ligand (salen), and the catalytic oxidation is realized by employing sacrificial oxygen sources such as peroxides, peroxy acids, or iodosylbenzene [8–13].

In enzymatic and synthetic oxidation catalysis, high-valent transition metal-oxo intermediates are generally produced and serve as the active oxygen atom transfer (OAT) species [9,14–19]. As such, extensive efforts have been directed to metalloporphyrins or metalloporphyrinoids as P450s models, and a variety of active metaloxo species were produced and characterized to elucidate the fundamental oxidation mechanism and reactive intermediates relevant to metalloenzymes [14,17,18,20]. In this regard, one particular interest in homogenous catalysis aims at developing photochemical methods to generate and study reactive metal-oxo species in their corresponding OAT reactions [21]. In contrast to most chemical methods involving the use of toxic and polluting reagents, photochemical generation of OAT species is obtained by the absorption of a photon, which leaves no byproducts [22,23]. The photochemical approach is particularly advantageous because it allows for superior temporal resolution than those of the fastest mixing experiments, which is essential to detect the generated transients [21,24,25]. In addition, photochemical production of the high-valent metal-oxo species allows real time studies of species under single turnover reactions with respect to the oxidant and pseudofirst-order kinetic conditions are readily maintained; this simplifies measurements of second- and higher-order rate constants and mechanistic deductions without kinetic convolution resulting from excess terminal oxidants [26-28]. As such, laser flash photolysis (LFP) techniques have been successfully introduced for generation and kinetic

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studies of a number of high-valent transition metal-oxo species in real time and their progress has previously been reviewed [21].

As the demand for green chemistry increases, the use of visible light (sunlight) rather than a chemical reagent with a photocatalyst offers an ideal means to harness solar energy in applied synthesis [29-31]. In this regard, the chemistry of cofacial µ-oxo dimeric complexes with different metals and macrocycles has received considerable attention due to their ability to develop green oxidation processes [32-34]. For examples, photo-disproportionation diiron(III)-µ-oxo bis-porphyrin complexes resulted in formation of iron(II) and iron(IV)-oxo porphyrin pair; the latter oxo species is capable of oxidizing organic substrates in a recycling base leading to catalytic aerobic oxidation [35]. A mixed uoxo bridged heme/non-heme diiron(III) complex also showed similar photo-oxidation manifold with the formation of iron(II) porphyrin and high-valent oxo species at non-heme iron [36]. The catalytic sequence is sustainable because it uses visible light to activate molecular oxygen for organic oxidations without the need for external coreductants. However, quantum yields of these processes are relatively low due to the recombination of iron(IV)-oxo and iron(II) species to reform the parent µ-oxo dimers. The catalytic efficiency was significantly improved by covalent linking "Pacman" architecture of diiron(III)-µ-oxo systems that employ organic spacer-hinges to pre-organize two iron centers in a cofacial arrangement [37-41]. This focused review describes our progress in the development of two distinct photochemical techniques, photo-induced ligand cleavage for direct production of high valent metal-oxo species and photo-disproportionation of a µ-oxo metal dimer to give a higher valence formal oxidation state of the metal-oxo intermediate (Scheme 1). A number of important metal-oxo intermediates with different metals and macrocyclic ligands apparently have been produced and studied in the real time. A special emphasis is also placed on the µ-oxo metal(IV) dimeric complexes as promising photocatalysts that undergo a photo-disproportionation sequence to generate a catalytically reactive metal(V)-oxo species for aerobic photo-oxidations.

2. Porphyrin-iron(IV)-oxo radical cations (compound I models) and porphyrin-iron(IV)-oxo species (compound II models)

High-valent porphyrin-iron-oxo intermediates are central oxidizing species in heme, non-heme iron enzymes and synthetic oxidation catalysts [42,43]. In heme-containing enzymes, an iron(IV)-oxo porphyrin radical cation species (commonly referred to as compound I) has been well characterized in the catalytic cycles of peroxidases, catalases, and chloroperoxidase [5,44-46]. Under experimental conditions, the treatment of cytochrome P450_{cam} with peroxy acid led to the rapid formation of a putative compound I species, which had spectral similarity with chloroperoxidase compound I species [47]. More advanced spectroscopic characterization and kinetic studies of compound I involved in cytochrome P450 enzymes were reported [48-51]. In model systems, compound I derivatives were also prepared and characterized from reactions of some porphyrin iron(III) salts with a sacrificial oxidant such as *m*-chloroperoxybenzoic acid (mCPBA) [52-55]. The preparation and characterization of the iron(IV)-oxo neutral porphyrins (compound II models), one-electron reduced forms of compound I, have also been known for decades [1,56]. The protonation state of compound II has generated considerable research interest because of its importance in determining compound I reactivity [57].

Recently, a photochemical entry to porphyrin-iron(IV)-oxo derivatives was reported in different electronic and steric environments (Scheme 2) [58,59]. In non-electron deficient ligand systems, visible light photolysis of porphyrin-iron(III) bromates or chlorates (1) afforded porphyrin-iron(IV)-oxo radical cations (2), i.e. compound I analogues (Fig. 1A). In contrast, photolysis of porphyrin-iron(III) bromates with electron-deficient and sterically encumbered ligands produced less oxidized iron(IV)-oxo porphyrins compound II models (3) (Fig. 1B). By comparison, irradiation of chlorate complexes [Fe^{III}(Por) (ClO₃)] (Por = porphyrin) was less efficient compared to that of bromates, and longer irradiation time was required for complete formation. Control experiments showed that no oxo species was formed in the absence of light.



Scheme 1. Photochemical generation of high-valent metal-oxo intermediates through (A) visible light-induced ligand cleavages and (B) photo-disproportionation reactions.



Scheme 2. A photochemical entry to porphyrin-iron(IV)-oxo radical cations and porphyrin iron(IV) neutral species controlled by porphyrin ligands.

Visible light generation of oxo 2 and 3 permits direct kinetic studies of their oxidations with organic reductants, and Fig. 1C illustrates the representative results of kinetic studies with the compound I analogue 2a. In the presence of an excess organic reductant, pseudo-first-order conditions were maintained, and the rate constant for decay of transient 2a increased linearly as a function of the concentration of reductant. The second-order rate constants for reactions of **2a** are $k_{ox} = (85 \pm 6)$ $M^{-1} s^{-1}$, $k_{ox} = (79 \pm 3) M^{-1} s^{-1}$, and $k_{ox} = (120 \pm 9) M^{-1} s^{-1}$ for cyclohexene, cis-cyclooctene, and cis-stilbene, respectively. The rate constants of photo-generated 2 are in a good agreement with those of iron(IV)-oxo derivatives formed by chemical methods [54]. The kinetics of OAT reactions with alkenes and aryl sulfides (thioanisoles) by photogenerated iron(IV)-oxo porphyrins (3e-g) were also studied in CH₃CN solutions [60]. As expected, the iron(IV)-oxo porphyrins (3) reacted 2-3 orders of magnitude slower than more oxidized porphyrin-iron(IV)-oxo radical cations (2). Of note, for a given substrate, the reactivity order for the iron(IV)-oxo species was 3 g < 3f < 3e, which is inverted with expectation on the basis of the electron-withdrawing of the porphyrin macrocycles [60,61]. This inverted reactivity has indicated that 3 undergoes a disproportionation reaction to generate a more reactive iron(IV)-oxo porphyrin radical cation (2) as the primary oxidant (Scheme 3). Importantly, recent reports provided direct spectroscopical evidence for the disproportionation reaction of 3 to 2 [62,63].

In order to determine the nature of the reactive intermediates in metal-catalyzed oxidation reactions, heterolytic versus homolytic cleavage of the metal bound terminal oxidant have been extensively investigated [64–67]. Visible light formation of iron(IV)-oxo species **2** and **3** can be rationalized by the following mechanism that involves a photo-induced *heterolytic* cleavage of the O-X bond of precursors **1** to generate a putative porphyrin-iron(V)-oxo species (**4**) (Scheme **4**) that

has not been experimentally detected. Similar heterolytic cleavage reactions were previously observed in photolyses of [Mn^{III}(Por)(ClO₄)] and heme iron(III)-hydroperoxo complexes, which resulted in the formation of [Mn^V(Por)(O)] species and high-valent iron(IV)-oxo heme cation radical intermediates, respectively [27,68]. The iron(V)-oxo 4 has been proposed to be an alternative reactive intermediate of some heme enzymes and model systems for decades [20]. In porphyrin and corrole complexes, computational studies [69,70] have suggested that the iron(V)-oxo species could be experimentally accessible. On the other hand, non-heme iron(V)-oxo intermediates have been reported to be the reactive intermediates in the Rieske dioxygenase enzymes and their synthetic functional models [71,72]. For instance, an iron(V)-oxo complex supported by a tetraanionic ligand showed truly unprecedented reactivity towards organic substrates [71,72]. The putative porphyrin/corrole-iron(V)-oxo transients in the synthetic models produced by LFP methods displayed an appropriate high level of reactivity [25,28,61]. A high-valent corrolazine-iron-oxo intermediate at the iron (V) oxidation level has also been spectroscopically characterized [73,74].

In non-electron-deficient porphyrin systems (**a-d**), the high-energy iron(V)-oxo species **4** could relax to compound I models (**2a-d**) through internal electron transfer (ET) from the porphyrin to the iron because it is thermodynamically favored (path a). However, the ET process from the highly electron demanding porphyrin (**e-f**) to the iron is apparently disfavored owing to a high redox potential. Instead, a fast comproportionation reaction of **4** with the residual iron(III) complex (*path b*) could generate iron(IV)-oxo derivatives (**3e-g**). Previous studies with manganese-oxo species found that porphyrin-manganese(V)-oxo species comproportionate rapidly with manganese(III) species [27], and corrole-manganese(V)-oxo species reacted with manganese(III) species



Fig. 1. (A) Time-resolved spectra of compound I 2a following irradiation of 1a with visible light in CH₃CN at 23 \pm 2 °C over 9 min. (B) Time-resolved spectra of forming compound II 3e following irradiation of 1e over 20 min. (C) Kinetic plots of the observed rate constants for the reaction of 2a versus the concentration of representative substrates: *cis*-stilbene (\blacksquare), cyclohexene (\bullet), and *cis*-cyclooctene (\bullet). Inset showing traces at 416 nm for formation of 1a with *cis*-cyclooctene at different concentrations.



to give manganese(IV)-oxo species [75]. The distinction between the two possibilities is determined by the electronic structure and/or redox potential of the porphyrin ligand, if any, for electron spin distribution of atomic orbitals and bond reorganizations needed to form the two species [20].

3. Porphyrin-manganese(IV)-oxo complexes

Manganese porphyrins have been extensively studied as P450s models in catalytic oxidations where highly reactive porphyrin-manganese(V)-oxo derivatives [26,27,76–78] have been proposed as the active oxidants for decades [79–81]. High-valent manganese-oxo species are also implicated in the production of oxygen in photosystem II in plants [82]. Unusual *trans*-dioxomanganese(V) porphyrins were also synthesized and characterized, which showed pH-dependent reactivities towards typical substrates [83]. In contrast, the well-characterized manganese(IV)-oxo porphyrins are less investigated due to their low reactivity [84–88]. In this context, two photo methods using visible light have been explored to produce and study a series of porphyrin-manganese(IV)-oxo species (Scheme 5).

The dimanganese(III)-µ-oxo bis-porphyrins (5a-c) in three sterically unencumbered porphyrin systems were synthesized according to a known procedure [89]. Upon visible light irradiation, direct conversion of dimers 5 to manganese(IV)-oxo porphyrins (6a-c) plus manganese(II) products (7) have been observed in benzene solutions (Scheme 5, path a) [90]. The initially formed manganese(II) species was rapidly oxidized to manganenes(III) porpyrins in the presence of O₂. When excess amounts of organic reductants such as cyclohexene were present, the UV-visible spectrum of **6a** returned to that of manganese(III) porphyrin (Fig. 2A). The overall reaction sequence is consistent for the behavior expected for porphyrin-manganese(IV)-oxo species. In addition, continuous irradiation of dimanganese(III) µ-oxo bis-porphyrins in the presence of pyridine (Py) or triphenylphosphine (Ph₃P) gave rise to the formation of stable [Mn^{II}(Por)(Py)] or [Mn^{II}(Por)(PPh₃)], respectively (Fig. 2B). These stable managnese(II) porphyrins were confirmed by independent production of the same compounds using the reported procedure [91]. The photochemical behavior of dimanganese(III) µ-oxo bis-porphyrins resembles the well-known photo-disproportionation of diiron(III) µ-oxo bis-porphyrins [35].

Alternatively, three Mn^{IV} -oxo complexes containing sterically hindered (**6d-f**) were also produced by the photo-induced ligand cleavage reactions (Scheme 5, path *b*) [92]. The systems under study include [Mn^{IV} (TPFPP)(O)] (TPFPP = 5,10,15,20-tetra(pentafluorphenyl)porphyrin) (**6d**), [Mn^{IV} (TDFPP)(O)] (TDFPP = 5,10,15,20-tetra(2,6-difluorphenyl)porphyrin) (**6e**), and [Mn^{IV} (TMP)(O)] (TMP = tetramesitylporphyrin) (**6f**) with different electronic nature. Visible light photolysis of the highly photo-labile porphyrin- Mn^{III} chlorate or bromate salts (**8d**) gave the Mn^{IV} -oxo **6d** through *homolytic* cleavage of the O-X (X = Cl or Br) bonds in the ligands (Fig. 3A), which was in accord with previous LFP studies [27]. The metastable photo-generated **6d** was further characterized by ESI-MS (inset of Fig. 3A). The same oxo species **6d** was also chemically generated by oxidation of corresponding manganese(III) precursor with PhI(OAc)₂, exhibiting same spectral signature characteristic for manganese(IV)-oxo porphyrin (Fig. 3B) [93].

As expected, complexes 6d-f reacted with thioanisoles to produce the corresponding sulfoxides and over-oxidized sulfones. The kinetics of sulfide oxidation reactions conducted in organic solvent revealed an unexpected low reactivity, comparable to those of alkene and activated hydrocarbon oxidations [92]. The order of reactivity for the [Mn^{IV}(Por) (O)] in the oxidation of sulfides is TPFPP (6d) > TDFPP (6e) > TMP(6f), which is consistent with expectation for electrophilic metal-oxo oxidants based on the electron-demand of the ligands [94]. The small second-order rate constants suggest the oxidation of highly nucleophilic sulfides by these [Mn^{IV}(Por)(O)] likely proceeds through a direct OAT mechanism via a manganese(II) intermediate that has been spectroscopically detected (path a in Scheme 6) [92]. However, it should be pointed out that an alternative pathway that involves a disproportionation of 6 to form a higher oxidized manganese(V)-oxo species may be significant when less reactive substrates are present (path b in Scheme 6) [27,87].

4. Relatively stable *trans*-dioxoruthenium(VI) and highly reactive ruthenium(V)-oxo porphyrins

The photo-induced ligand cleavage reactions were expanded to synthesize the *trans*-dioxoruthenium(VI) porphyrins [95], which are structurally well-defined model systems for heme-containing enzymes [96,97]. Refluxing readily available ruthenium(II) carbonyl porphyrins



Scheme 4. A proposed mechanism for photochemical generation of porphyrin-iron(IV)-oxo compound I and compound II species.



Scheme 5. Two-route photochemical generation of porphyrin- Mn^{IV} -oxo complexes.

in carbon tetrachloride afforded dichlororuthenium(IV) complexes [Ru^{IV}(Por)Cl₂] (9). Facile exchange of the counterions in [Ru^{IV}(Por)Cl₂] with Ag(XO₃) (X = Cl or Br) gave the corresponding salts [Ru^{IV}(Por) (XO₃)₂] (10). Similar to the previously described photochemical homolysis of porphyrin-manganese(III) chlorates, the visible light photolysis of ruthenium(IV) dihalorates (10) produced trans-dioxo species (11) as a result of the simultaneous cleavages of two X-O bonds. This photo-protocol has demonstrated a good generality, and trans-dioxoruthenium(VI) porphyrins were formed in sterically encumbered, unencumbered, and chiral porphyrin systems (Scheme 7) [98]. With tunable structural and electronic properties, the kinetic studies of the OAT reactions from **11** to organic sulfides were conducted [99]. Typical second-order rate constants for sulfoxidation reactions are $8-60 \text{ M}^{-1} \text{ s}^{-1}$, which are 3 orders of magnitude larger in comparison with those of well-studied alkene epoxidations and activated C-H bond oxidations by the same dioxo species [100]. For a given sulfide substrate, the reactivity order for the dioxoruthenium(VI) species 11 is in agreement with expectation on the basis of the electron-withdrawing and steric effects of the porphyrin macrocycles.

Porphyrin-ruthenium(V)-oxo complexes are rare but attractive OAT candidates for catalytic oxidations [101–103]. These species are proposed intermediates in very efficient oxidation processes, although not yet observed directly [102,104–106]. Computational studies suggest that they are thermodynamically stable with respect to ruthenium(IV)-oxo porphyrin radical cations [107]. Recently, spectroscopic evidence including UV–vis, ESI-MS, electron paramagnetic resonance (EPR), resonance Raman (RR) along with kinetic and computational studies have been reported to support the formation of the highly reactive ruthenium (V)-oxo species as the active oxidant in the ruthenium(III) porphyrin-

catalyzed oxidations [108]. In this regard, photochemical reactions provided two entries to the porphyrin-ruthenium(V)-oxo species (Scheme 8). Firstly, photo-disproportionation of a bis-porphyrin-diruthenium(IV) µ-oxo dimer (12) in LFP studies provided a fast access to the reactive OAT species (13) that was tentatively assigned as the putative porphyrin-ruthenium(V)-oxo intermediate(Fig. 4A) [109]. Secondly, the same oxo transient 13 was also observed by the photocleavage of a ruthenium(III) N-oxide adduct (14) that proceeded with a heterolytic cleavage of Ru–O bond (Fig. 4B) [110]. Noteworthy is that the UV-vis spectra and kinetic behaviors of transients generated from the two routes are indistinguishable. Second-order rate constants for direct reactions of 13 with several substrates at 22 °C were determined (Fig. 4C); representative values of rate constants were s^{-1} 10^{3} M^{-1} diphenylmethanol, = 6.6 X for $k_{\rm ox}$ M^{-1} s^{-1} 10³ 1.8 for cyclohexene х and $k_{\rm ox}$ $k_{\rm ox} = 1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for *cis*-cyclooctene. By comparison, the photo-generated 13 reacted 5-6 orders of magnitude faster than the corresponding trans-dioxoruthenium(VI)-oxo porphyrins, but 2 orders of magnitude less reactive than the putative 5,10,15,20-tetraphenylporphyrin-iron(V)-oxo complex [25]. This is in agreement with the general observation that porphyrin-ruthenium-oxo complexes are expected to be more stable than the corresponding iron-oxo analogues. Importantly, species 13 is much more reactive than the corresponding iron(IV)-oxo porphyrin radical cations [54]. The high reactivity for the photochemically generated 13 in comparison to other porphyrin-metaloxo intermediates suggests that it is a true ruthenium(V)-oxo species [110].



Fig. 2. (A) Time-resolved spectra for reaction of photo-generated **6a** with 0.5 M cyclohexene in benzene over 220 s; the inset shows the kinetic trace at 420 nm in the absence (self-decay) and presence of cyclohexene (0.5 M). (B) Time-resolved spectra of $[Mn^{II}(4-CF_3TPP)(Py)]$ generated by visible light irradiation of **5a** in the presence of pyridine (3 mM).



Fig. 3. (A) Time-resolved spectra of **6d** following irradiation of $[Mn^{III}(TPFPP)(ClO_3)]$ with visible light (120 W) in CH₃CN solution at 23 ± 2 °C over 5 s; Inset showing the ESI-MS of **6d** in a positive mode; (B) Time-resolved spectra of **6d** following oxidation of **8d** with PhI(OAc)₂ (10 equiv.) over 4 s in CH₃CN.

5. Corrole-manganese(V)-oxo complexes

Corroles are tri-anionic porphyrin analogues, which stabilize higher metal oxidation states. Accordingly, the relatively stable manganese(V)oxo corroles, denoted as $[Mn^{V}(Cor)O]$ (Cor = corrole) (15), have been synthesized and characterized as active OAT species [111]. Nevertheless, the reactions of [Mn^V(Cor)O] are mechanistically complex [75,112] and factors controlling their OAT reactivity with organic substrates are not fully understood [13]. To this end, [Mn^V(Cor)O] were photochemically generated under visible light irradiation and their kinetic studies of OAT reactions were directly investigated [113,114]. Similar to previously described porphyrin-Mn^{III}(ClO₃) and porphyrin- $Ru^{IV}(XO_3)_2$ (X = Cl and Br) [27,92,95], visible light irradiation of highly photo-labile manganese(IV) precursors [Mn^{IV}(Cor)(XO₃)] (X = Cl and Br) (16) in anaerobic CH₃CN resulted in formation of [Mn^V (Cor)O] (15) in three different electronic environments (Scheme 9). The spectra of visible light generated 15 matched those reported previously from chemical oxidation methods [115]. Apparently, visible light irradiation of 16 results in one-electron photo-oxidation to afford 15 by homolysis of O-X bond. For comparison, photochemical cleavages of the nitrite precursors [Mn^{IV}(Cor)(NO₂)] were considerably more efficient than those of [Mn^{IV}(Cor)(XO₃)] to form the same corrole-manganese(V)-oxo species [114].

The kinetics of OAT reactions with various organic reductants by these photo-generated $[Mn^{V}(Cor)O]$ were carried out in CH₃CN and CH₂Cl₂ solutions. It was found that $[Mn^{V}(Cor)O]$ exhibited remarkable

solvent and ligand effects on its reactivity and spectral behavior. In the electron-deficient system (a) and in the polar solvent CH_3CN , $[Mn^V (Cor)O]$ (15a) returned Mn^{III} corrole in the end of the oxidation reactions (Fig. 5A). However, in the less polar solvent CH_2Cl_2 or in the non-electron-deficient systems (b and c), Mn^{IV} product was formed instead (Fig. 5B). Furthermore, with the same substrates and in the same solvent, the order of reactivity of $[Mn^V(Cor)O]$ was 15c > 15b > 15a, which is inverted from the expectation based on the electron-demand of the corrole ligands. Spectral and kinetic results in this study are consistent with multiple oxidation pathways, where 15 either serves as direct two-electron oxidant or undergoes a disproportionation reaction to form a manganese(IV) and manganese(VI)-oxo corrole, the latter of which serves as the primary oxidant. The choice of oxidation pathways is strongly dependent on the nature of the solvent and the electronic properties of the corrole ligands (Scheme 9).

6. Salen-chromium(V)-oxo complexes

Metallosalen complexes (salen = N,N'-bis(salicylidene)ethylenediamine) have received much attention in view of their enormous utility of catalytic transformations [116–119]. With a tetradentate-binding motif, metallosalens show catalytic features in common with metalloporphyrins [11]. Chromium–salen complexes are the first application of metallosalens in catalysis. In addition, salens are more easily manipulated to create an asymmetric environment around the active metal site than porphyrin analogues [11,120]. In the 1990s, the groups of



Scheme 6. A proposed OAT mechanism of species 6 involving (a) direct OAT to sulfides and (b) alternative disproportionation pathway with less reactive substrates.



Scheme 7. Photosynthesis of trans-dioxoruthenium(VI) porphyrins.



Scheme 8. Two photochemical entries to generate the elusive porphyrin-ruthenium(V)-oxo species.

Jacobsen and Katsuki independently introduced chiral manganese–salen catalysts to achieve highly enantioselective epoxidations [121,122]. Under catalytic conditions, the chromium(III)–salen is readily oxidized to the corresponding chromium(V)-oxo species, which has been isolated and fully characterized by various spectroscopic methods including a single crystal X-ray crystallography [116]. A recent progress was reported on visible light-generation of chromium(V)-oxo complexes (19) bearing the well-known Jacobsen salen ligand and one of its derivatives (Scheme 10) [123]. The results for the first time attest to the fact that photochemical production of metal-oxo species is not exclusive to porphyrin or corrole systems, and it can be achieved using simple, easily constructed salen-based complexes.

Facile exchange of the axial ligand in $[Cr^{III}(salen)Cl]$ (17) with Ag (XO₃) (X = Cl and Br) gave the corresponding chlorate $[Cr^{III}(salen)$ (XO₃)] (18), and its formation was indicated by the UV-vis spectra (Fig. 6A). Visible light irradiation of the photo-labile chlorate or bromate precursor in CH₃CN solution gave a reactive transient with a

characteristic absorption spectrum of $[Cr^{V}(salen)O]$ (**19**) (Fig. 6A). The photo-generated **19** were stable enough to be further characterized by ESI-MS, matching the molecular composition of $[Cr^{V}(salen)(O)]$. In addition, the photo-generated $[Cr^{V}(salen)O]$ is spectroscopically indistinguishable from the species formed by the chemical oxidation of chromium(III) **17** with PhI(OAc)₂ [123]. Apparently, the generation of the chromium(V)-oxo species (**19**) upon visible light irradiation of chlorate or bromate (**18**) can be ascribed to a photo-induced *heterolytic* cleavage of O-X (X = Cl or Br) bonds in the apical counterion, which results in two-electron photo-oxidation reactions accordingly. Again, photochemical cleavage of chlorate complexes was considerably more efficient than cleavages of chlorate complex to generate the salen-chromium(V)-oxo species under identical conditions, similar to previously reported work on the photochemical formation of *trans*-dioxoruthenium(VI) porphyrins [98] and iron-oxo porphyrins [59].

When organic substrate such as cyclohexene was present (Fig. 6B), the decay of the photo-generated species at its characteristic broad peak



Fig. 4. (A) Time-resolved *difference* spectra following LFP of **12** over 50 ms in the presence of benzophenone (10 mM) in CH₃CN at 22 °C; difference spectrum = spectrum(*t*) - spectrum (final = 50 ms). (B) Time-resolved difference spectra following LFP of species **14** over 100 ms in CH₂Cl₂ at 22 °C. (C) Representative plots of observed pseudo-first-order rate constants in CH₃CN for reactions of **13** versus concentrations of diphenylmethanol, cyclohexene, and *cis*-cyclooctene.



Scheme 9. Two oxidation pathways of visible light-generated [Mn^V(Cor)O].



Fig. 5. Time-resolved spectra of **15a** reacting (A) in CH₃CN with cyclohexene (0.5 M) over 15 min. Inset shows kinetic traces for decay of **15a** at 348 nm and formation of Mn^{III} at 465 nm over 15 min. (B) In CH₂Cl₂ with cyclohexene (0.5 M) over 5 min. Inset shows decay of **15a** at 346 nm and formation of Mn^{IV} at 430 nm over 5 min.

with λ_{max} at 680 nm accelerated linearly with the substrate concentration (Fig. 6C). The plot slope gave a second-order rate constant of (8.7 \pm 0.9) \times 10⁻³ M⁻¹ s⁻¹. The identical k_{ox} value for cyclohexene was also obtained with **19a** produced from the chemical method, kinetically confirming that the same oxo species is formed from both methods. In metal-oxo chemistry, electrophilic metal-oxo species typically exhibit a remarkable rate acceleration of sulfide oxidation versus hydrocarbons due to the enhanced nucleophilicity and easy access of

sulfur for oxidation. For example, iron(IV)-oxo porphyrins [60] and manganese(V)-oxo corroles [113] showed that sulfoxidation reactions were 3 to 4 orders of magnitude faster than those alkene and activated C–H bonds oxidations by the same oxo species. Surprisingly, the k_{ox} values determined in this work for thioanisole oxidation ranged from 0.3×10^{-3} to 1.1×10^{-3} M⁻¹ s⁻¹, a unexpected lower level of reactivity in comparison to alkenes or benzylic alcohols [123]. Presumably, the strong coordination of the sulfides to the metal center



Scheme 10. Visible light-induced formation of salen-chromium(V)-oxo complexes.

suppressed the reactivity of electrophilic salen-chromium(V)-oxo species.

Similar to previously reported catalytic oxidations [124,125], chromium(III) salen complexes (17) effectively catalyzed the oxidation of aryl sulfides into sulfoxides with PhI(OAc)₂ in the presence of a small amount of water. As described early, PhI(OAc)₂ was able to oxidize the chromium(III) complexes (17) to produce salen-chromium(V)-oxo 19, which then reacted with substrate and decayed back to chromium(III) product. However, the directly observed salen-chromium(V)-oxo species 19 in kinetic studies is not necessarily the active oxidant under catalytic turnover conditions. As shown in competition studies, the ratios of absolute rate constants found in direct kinetic studies differed dramatically from the oxidation ratios for competition oxidation reactions of the two substrates under turnover conditions [123]. This observation implied that the directly observed chromium(V)-oxo species 19 may still be a reactive oxidant provided that the reaction of chromium(III) salens with PhI(OAc)₂ is the rate limiting step of the catalytic reaction. Alternatively, the chromium(V)-oxo salen may function as Lewis acid to activate the PhI(OAc)₂ in a similar way as the corralizinemanganese(V)-oxo served in the catalytic sulfoxidation with PhIO [126].

7. Photocatalytic aerobic oxidations via a disproportionation pathway

Our prior works have shown that the highly reactive corrole-iron (V)-oxo and porphyrin-ruthenium(V)-oxo intermediates can be accessed by photo-disproportionation of the corresponding metal(IV) µoxo dimers [109,127]. The possibility of employing these systems for photocatalytic aerobic oxidations is particularly attractive. Clearly, the regeneration of the µ-oxo dimers by molecular oxygen is essential to realize the proposed photocatalytic cycle. In this regard, the photochemistry of a fluorinated iron(IV) µ-oxo bis-corrole [Fe^{IV}(TPFC)]₂O (TPFC = 5,10,15-tripentafluorophenylcorrole, 20) (20) appears to present a photo-disproportionation manifold similar to that of the iron porphyrin systems [127]. A visible-light driven aerobic oxidation of hydrocarbons was catalyzed by a bis-corrole-iron(IV) µ-oxo complex (20) using only molecular oxygen without the need for an external reducing reagent [128]. The proposed catalytic sequence involves the following: 1) photo-disproportionation of the µ-oxo iron(IV) bis-corrole to form iron(III) and iron(V)-oxo oxidizing species (21); 2) substrate oxidation by the resulting reactive iron(V)-oxo species to give oxidized products and a second iron(III) species (22); 3) aerobic oxidation of iron (III) complex to regenerate the µ-oxo iron(IV) dimer (Scheme 11). Although the oxidation of 22 by O_2 to form the μ -oxo 20 has been known



Fig. 6. (A) UV–vis spectra of $[Cr^{III}(salen)Cl]$ (**17***a*, dotted line), $[Cr^{III}(salen)(ClO_3)]$ (**18***a*, dashed) and $[Cr^{V}(salen)O]$ (**19***a*, solid) in CH₃CN; (B) Time-resolved spectra of the photo-generated $[Cr^{V}(salen)O]$ **19a** reacting with cyclohexene (0.15 M); (C) Kinetic plot of observed rate constants versus concentration of cyclohexene. Inset shows the decay at 680 nm with different concentrations of cyclohexene.



Scheme 11. A proposed catalytic cycle for the photocatalytic aerobic oxidations by the diiron (IV) μ-oxo *bis*-corrole. The scheme also shows formation of the same oxidizing corrole-iron(V)-oxo species (21) by photolysis of iron(IV) chlorate monomer (23) [28].

for some time [129], the detailed mechanism has hitherto apparently not been fully disclosed. It is worth mentioning, that electron-withdrawing substituents such as F on corrole ligand are necessary to reform μ -oxo dimer formation in the aerobic solution. Using the same procedure by reacting the iron(III) complex with a non-halogenated 5,10,15triphenylcorrole; i.e. [Fe^{III}(TPC)] in air did not give the corresponding μ -oxo products [128]. Presumably, the electron-withdrawing substituents would stabilize the iron(IV) complex in a dimeric form by reducing the electron density of metal atoms.

Given the periodic relationship between ruthenium and iron and the nature of the similar macrocyclic system, the photo-disproportionation of diruthenium(IV)-µ-oxo bis-porphyrins (12) was also found to produce the terminal ruthenium(V)-oxo intermediate with the concomitant formation of ruthenium(III) porphyrin species, as described in Scheme 8 [109]. Of note, the reaction of molecular oxygen with ruthenium(III) porphyrin was able to reproduce stable µ-oxo Ru^{IV} species possibly through a peroxo-bridged dimeric intermediate [35,130]. The diruthenium(IV)-µ-oxo-bis-[5,10,15,20-tetraphenylporphyrin] precursor $[Ru^{IV}(TPP)(OH)]_2O$ (12a) with λ_{max} at 395 nm was initially synthesized according to the known literature [131,132]. The initial hydroxyl axial ligand was easily replaced with chloride anions that gave a µ-oxo complex formulated as [Ru^{IV}(TPP)Cl]₂O. In a similar way, another two dimer complexes, formulated as [Ru^{IV}(4-CF₃-TPP)OH]₂O (12b) and [(Ru^{IV}(4-MeO-TPP)OH]₂O (12c), were made and characterized by UV-vis, ¹H NMR, and IR spectra (Scheme 12).

As shown in the Scheme 11, the photo-disproportionation reaction of diiron(IV)- μ -oxo *bis*-corrole (20) becomes catalytic in the presence of O₂. The potential of photo-disproportionation of μ -oxo iron(IV) *bis*corrole for a light-driven oxidation catalysis was first evaluated in the aerobic oxidation of *cis*-cyclooctene (Table 1). After 72 h of photolysis with visible light, *cis*-cyclooctene oxide was obtained as the only identifiable oxidation product (> 95% by GC) with 540 turnovers of catalyst (entry 1). Since metalloporphyrins are known to display superior oxidative robustness than metallocorroles, a set of ruthenium (IV)- μ -oxo *bis*-porphyrins was subsequently evaluated in the aerobic oxidation of cis-cyclooctene. Inspection of the screening results in Table 1 reveals that these ruthenium(IV) µ-oxo bis-porphyrins (12) catalyze the aerobic oxidation of *cis*-cyclooctene to the corresponding epoxide. Again, epoxide (> 95%) was the only identifiable product in most runs. The substituents in the porphyrin ligand displayed a noticeable effect on the catalytic activity (entries 2, 6, and 7), i.e. the most electron demanding system, namely [Ru^{IV}(4-CF₃TPP)OH]₂O (12b), was the most efficient catalyst. The use of CHCl₃ as solvent instead of CH₃CN resulted in a lower TON (entry 3). Quite surprisingly, the axial ligand on the metal has a significant effect and the [Ru^{IV}(TPP)Cl]₂O (entry 5) gave a much lower activity compared to [Ru^{IV}(TPP)OH]₂O. Although the catalyst degradation is a problem with higher-energy light, the use of UV irradiation increased the catalytic activity (entries 4 and 9) possibly due to higher photon flux expected from UV light. Particularly noteworthy is that the catalytic activity can be enhanced by adding small amount of anthracene that possibly acts as a photosensitizer (entry 8). Similarly, a hybrid P450 enzyme with a ruthenium (II)-containing photosensitizer is able to catalyze the efficient lightdriven hydroxylations [133]. By comparison, the well-known diiron (III)-µ-oxo bis-porphyrin complex [Fe^{III}(TPP)]₂O and trans-dioxoruthenium(VI) tetramesitylporphyrin [Ru^{VI}(TMP)O₂] showed comparatively low catalytic activities under the same conditions (entries 10 and 11).

Under optimized conditions, the substrate scope of the photocatalytic aerobic oxidation was explored by using $[Ru^{IV}(TPFP)OH]_2O$ and $[Fe^{IV}(TPFC)]_2O$ as photocatalysts, respectively (Table 2). The photocatalytic methodology is applicable for a range of alkenes, activated hydrocarbons and alcohols. Norbornene was oxidized to the corresponding epoxide whereas cyclohexene was mainly oxidized to the allylic oxidation products 2-cyclohexenol and 2 cyclohexenone with minor epoxide(entries 1 and 2). Activated hydrocarbons including Ph₃CH, Ph₂CH₂, PhEt and xanthene were oxidized to the corresponding alcohols and ketones, and catalytic activities correlated well with the substrate reactivity of benzylic C–H bonds (entries 3–6). The highest activity with 3900 TON was achieved for 9-xenthenol (entry 8). In





Ar = C_6H_5 , [(Ru^{IV}(TPP)OH)₂O], 12a = 4-CF₃-C₆H₄, [(Ru^{IV}(4-CF₃TPP)OH)₂O], 12b = 4-MeO-C₆H₄, [(Ru^{IV}(4-MeOTPP)OH)₂O], 12c = C_6F_5 , [(Ru^{IV}(TPFPP)OH)₂O], 12d

[(Fe^{IV}(TPFC)₂O], 20

Scheme 12. Structures and abbreviations of µ-oxo dimetal(IV) photocatalysts.

Table 1 Aerobic catalytic oxidation of *cis*-cyclooctene with dimetal(IV) μ-oxo complexes ^a

Entry	Catalyst	Solvent	Light source	Time (day)	TON ^b
1	[Fe ^{IV} (TPFC)] ₂ O	CH ₃ CN	Visible	3	540 ± 40
2	[Ru ^{IV} (TPP)OH] ₂ O	CH ₃ CN	Visible	1	220 ± 16
				2	460 ± 40
				3	640 ± 65
3		$CHCl_3$	Visible	1	110 ± 18
4		CH_3CN	UV	1	340 ± 8
5	[Ru ^{IV} (TPP)Cl] ₂ O	CH_3CN	Visible	1	75 ± 5
6	[Ru ^{IV} (4-MeO-TPP)	CH_3CN	Visible	1	190 ± 23
	OH] ₂ O				
7	[Ru ^{IV} (4-CF ₃ -TPP)	CH_3CN	Visible	1	250 ± 21
	OH] ₂ O				
8 ^c			Visible	1	340 ± 9
9		CH_3CN	UV	1	520 ± 12
10 ^d	[Fe ^{III} (TPP)] ₂ O	CH_3CN	Visible	1	40 ± 5
11	[Ru ^{VI} (TMP)O ₂]	CH_3CN	Visible	1	30 ± 10

 a The reaction was carried out in a Rayonet reactor, typically with 0.5 μmol of catalyst in 10 mL of solvent containing 4 mmol of *cis*-cyclooctene. The oxygen-saturated solution was irradiated with visible lamp ($\lambda_{max}=420$ nm) or UV lamp ($\lambda_{max}=350$ nm). Products were analyzed by GC with DB-5 capillary column with internal standard.

^b TON represents the total number of moles of product produced per mole of catalyst.

^c 5 mg of anthracene was added.

^d Enone formation (\sim 20%) was detected.

general, $[Ru^{IV}(4-CF_3TPP)OH]_2O$ shows superior activity compared to $[Fe^{IV}(TPFC)]_2O$ which has an enhanced electron-demanding nature, because the corrole catalyst is less robust, and often suffers from catalytic bleaching [109,128].

8. Conclusion

Photochemical production of high-valent transition metal-oxo derivatives using visible light appears to be promising and have general synthetic utility. Over the past decade, the visible light-induced ligand cleavage reactions have been utilized to produce and elucidate a variety of important and well-known metal-oxo intermediates including manganese(V)oxo/manganese(IV)-oxo porphyrins, iron(IV)-oxo porphyrin radical cations and iron(IV)-oxo neutral porphyrins, *trans*-dioxoruthenium(VI) porphyrins, manganese(V)-oxo corroles, and chromium(V)-oxo salens. Previously unknown high-valent metal(V)-oxo species, possibly iron(V)oxo corroles and ruthenium(V)-oxo porphyrins, apparently already have been produced by the photo-induced ligand cleavage and photo-disproportionation reactions. Certainly, complete identification of these photo-generated metal-oxo species requires other spectroscopic methods such as resonance Raman and EPR, which will be the direction for the future work. Upon photochemical production of these reactive metal-oxo transients, the kinetics of their oxidation reactions under easily established pseudo-first-order conditions have provided mechanistic insights into the identities of the active oxidants and oxidation reaction pathways of important catalysts. With visible light, a series of diruthenium(IV) µ-oxo bisporphyrins and a diiron(IV) u-oxo bis-corrole catalyzed the demanding aerobic oxidation of hydrocarbons through a photo-disproportionation pathway that provides a rare access to the highly reactive metal(V)-oxo oxidants. This approach is particularly attractive to realize innovative oxidation processes and, at the same time, to move towards "sustainable chemistry". Most of the achieved results in this review have provided a solid foundation to design new photo-protocols to generate active metaloxo species with emphasis on the need for more efficient photocatalysts for sustainable aerobic oxidations.

Abbreviations

CYP450s	cytochrome P450 enzymes			
Cor	corrole			
m-CPBA	meta-chloroperoxybenzoic acid			
EPR	electron paramagnetic resonance			
ESI-MS	electron spray ionization-mass spectrometry			
ET	electron transfer			
LFP	laser flash photolysis			
OAT	oxygen atom transfer			
Por	porphyrin			
S	substrate			
SO	oxidized product			
salen	N,N'-bis(salicylidene)ethylenediamine			
TDCPP	5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin			
TDFPP	5,10,15,20-tetra(2,6-difluorophenyl)porphyrin			
ТМР	tetramesitylporphyrin			
ΓΟΝ	turnover number			
ГРС	5,10,15-triphenylcorrole			
TPFC	5,10,15-tripentafluorophenylcorrole			
ТРР	tetraphenylporphyrin			
TPFPP	5,10,15,20-tetra(pentafluorphenyl)porphyrin			

Entry	Substrate	Product	TON ^b	TOND
Linuy	Substrate	rioduci		
			[Ru ^{rv} (4-CF ₃ TPP)OH] ₂ O	$[(Fe^{(1PFC)}]_{2}O$
1°			200 ± 40	72 ± 6
		120		
2		Cyclohexene oxide	30 ± 3	40 ± 4
		2-Cyclohexenol	160 ± 14	230 ± 24
		2-Cyclohexenone	350 ± 31	102 ± 16
3	Ph ₃ CH	Ph ₃ COH	1120 ± 48	380 ± 40
4	Ph ₂ CH ₂	ОН	820 ± 102	700 ± 47
		Ph		
		0 II	140 ± 18	220 ± 20
		Ph	140 ± 10	220 ± 20
5	PhCH ₂ CH ₃	ОН	380 ± 41	80 ± 5
		Ph		
		Ph	180 ± 19	10 ± 2
6		0	2900 ± 140	1235 ± 120
7	он	0 0	3300 ± 240	1300 ± 140
	Ph	Ph		
8	ОН	0 II	3900 ± 280	1580 ± 175

Table 2 Photocatalytic aerobic oxidations of alkenes and benzylic C–H oxidations.^a

^aTypically with 0.5 µmol of catalyst in 5 mL of CH₃CN containing 4–6 mmol of substrate and ca. 5 mg anthracene. The oxygen-saturated solution was irradiated for a 24 h photolysis with a Rayonet reactor (λ_{max} = 420 nm, ca. 300 W). Products were analyzed by Agilent GC(6890)-MS(5973) using DB-5 column with an internal standard. ^bTON represents the total number of moles of product produced per mole of catalyst, which was determined. ^c > 90% *exo* isomer.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] X. Huang, J.T. Groves, Chem. Rev. 118 (2018) 2491–2553.
- [2] J.E. Baeckvall, Modern Oxidation Methods, Wiley-VCH Verlag, Weinheim, 2004.
- [3] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329–2363.[4] P.R. Ortiz de Montellano, Cytochrome P450 Structure, Mechanism, and
- Biochemistry, Kluwer Academic/Plenum, New York, 2005.[5] I.G. Denisov, T.M. Makris, S.G. Sligar, I. Schlichting, Chem. Rev. 105 (2005)
- [3] 1.4. Denisov, 1.M. Makris, 3.4. Singar, 1. Schnehung, Chem. Rev. 105 (2005) 2253–2277.
- [6] M.M. Pereira, L.D. Dias, M.J.F. Calvete, ACS Catal. 8 (2018) 10784–10808.
- [7] S. Sahu, D.P. Goldberg, J. Am. Chem. Soc. 138 (2016) 11410-11428.
- [8] B. Meunier, Chem. Rev. 92 (1992) 1411-1456.
- [9] M. Costas, M.P. Mehn, M.P. Jensen, L. Que, Chem. Rev. 104 (2004) 939–986.
- [10] Z. Gross, H.B. Gray, Adv. Syn. Catal. 346 (2004) 165–170.
- [11] E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (2005) 1563-1602.
- [12] A.B. Sorokin, Chem. Rev. 113 (2013) 8152–8191.
- [13] H.-Y. Liu, M.H.R. Mahmood, S.-X. Qiuc, C.K. Chang, Coord. Chem. Rev. 257 (2013) 1306–1333.
- [14] B. Meunier, Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations, Springer-Verlag, Berlin, 2000.
- [15] W. Nam, Acc. Chem. Res. 40 (2007) 522–531.
- [16] C.M. Krest, E.L. Onderko, T.H. Yosca, J.C. Calixto, R.F. Karp, J. Livada, J. Rittle, M.T. Green, J. Biol. Chem. 288 (2013) 17074–17081.
- [17] R.A. Baglia, J.P.T. Zaragoza, D.P. Goldberg, Chem. Rev. 117 (2017) 13320–13352.
- [18] M. Guo, T. Corona, K. Ray, W. Nam, ACS Cent. Sci. 5 (2019) 13-28.
- [19] H.B. Gray, J.R. Winkler, Acc. Chem. Res. 51 (2018) 1850–1857.

- [20] H. Fujii, Coord. Chem. Rev. 226 (2002) 51-60.
- [21] R. Zhang, M. Newcomb, Acc.Chem. Res. 41 (2008) 468-477.
- [22] T.P. Yoon, M.A. Ischay, J. Du, Nature Chem. 2 (2010) 527–532.
- [23] M.E. Ener, Y.-T. Lee, J.A. Winkler, H.B. Gray, L. Cheruzel, Proc. Natl. Acad. Sci. U. S. A. 107 (2010) 18783–18786.
- [24] M. Newcomb, R. Zhang, R.E.P. Chandrasena, J.A. Halgrimson, J.H. Horner, T.M. Makris, S.G. Sligar, J. Am. Chem. Soc. 128 (2006) 4580–4581.
- [25] Z. Pan, Q. Wang, X. Sheng, J.H. Horner, M. Newcomb, J. Am. Chem. Soc. 131 (2009) 2621–2628.
- [26] R. Zhang, M. Newcomb, J. Am. Chem. Soc. 125 (2003) 12418–12419.
- [27] R. Zhang, J.H. Horner, M. Newcomb, J. Am. Chem. Soc. 127 (2005) 6573–6582.
 [28] D.N. Harischandra, R. Zhang, M. Newcomb, J. Am. Chem. Soc. 127 (2005)
- 13776–13777.
- [29] H. Hennig, Coord. Chem. Rev. 182 (1999) 101–123.
- [30] D.G. Nocera, Acc. Chem. Res. 45 (2012) 767-776.
- [31] D.G. Nocera, Acc. Chem. Res. 50 (2017) 616-619.
- [32] J.P. Collman, P.S. Wagenknecht, J.E. Hutchison, Angew. Chem. 106 (1994) 1620–1639.
- [33] J. Rosenthal, J. Bachman, J.L. Dempsey, A.J. Esswein, T.G. Gray, J.M. Hodgkiss, D.R. Manke, T.D. Luckett, B.J. Pistorio, A.S. Veige, D.G. Nocera, Coord. Chem. Rev. 249 (2005) 1316–1326.
- [34] A.B. Sorokin, Coor. Chem. Rev. 389 (2019) 141-160.
- [35] M.W. Peterson, D.S. Rivers, R.M. Richman, J. Am. Chem. Soc. 107 (1985) 2907–2915.
- [36] I.M. Wasser, H.C. Fry, P.G. Hoertz, G.J. Meyer, K.D. Karlin, Inorg. Chem. 43 (2004) 8272–8281.
- [37] C.J. Chang, E.A. Baker, B.J. Pistorio, Y. Deng, Z.-H. Loh, S.E. Miller, S.D. Carpenter, D.G. Nocera, Inorg. Chem. 41 (2002) 3102–3109.
- [38] B.J. Pistorio, C.J. Chang, D.G. Nocera, J. Am. Chem. Soc. 124 (2002) 7884–7885.
- [39] J. Rosenthal, B.J. Pistorio, L.L. Chng, D.G. Nocera, J. Org. Chem. 70 (2005) 1885–1888.
- [40] J. Rosenthal, T.D. Luckett, J.M. Hodgkiss, D.G. Nocera, J. Am. Chem. Soc. 128 (2006) 6546–6547.
- [41] T. Guchihait, S. Sasmal, F.S.T. Khan, S.P. Rath, Coor. Chem. Rev. 337 (2017) 112–144.
- [42] Y. Watanabe, H. Fujii, Characterization of high-valent oxo-metalloporphyrins, in: B. Meunier (Ed.), Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations, Springer-Verlag, Berlin, 2000, pp. 61–89.
- [43] A.R. McDonald, L. Que, Coord. Chem. Rev. 257 (2013) 414-428.
- [44] J.H. Dawson, Science 240 (1988) 433-439.
- [45] M. Sono, M.P. Roach, E.D. Coulter, J.H. Dawson, Chem. Rev. 96 (1996) 2841–2887.
- [46] R. Zhang, N. Nagraj, D.S.P. Lansakara-P, L.P. Hager, M. Newcomb, Org. Lett. 8 (2006) 2731–2734.
- [47] T. Egawa, H. Shimada, Y. Ishimura, Biochem. Biophys. Res. Commun. 201 (1994) 1464.

- [48] D.G. Kellner, S.-C. Hung, K.E. Weiss, S.G. Sligar, J. Biol. Chem. 277 (2002) 9641.
- [49] J. Rittle, M.T. Green, Science 330 (2010) 933-937.
- [50] C.M. Krest, A. Silakov, J. Rittle, T.H. Yosca, E.L. Onderko, J.C. Calixto, M.T. Green, Nat. Chem. 7 (2015) 696-702.
- [51] T.H. Yosca, M.T. Green, Isr. J. Chem. 56 (2016) 834-840.
- [52] J.T. Groves, R.C. Haushalter, M. Nakamura, T.E. Nemo, B.J. Evans, J. Am. Chem. Soc. 103 (1981) 2884-2886.
- [53] H. Fujii, J. Am. Chem. Soc. 115 (1993) 4641-4648.
- [54] Z. Pan, R. Zhang, M. Newcomb, J. Inorg. Biochem. 100 (2006) 524-532.
- [55] S.R. Bell, J.T. Groves, J. Am. Chem. Soc. 131 (2009) 9640-9641.
- [56] J.T. Groves, Z. Gross, M.K. Stern, Inorg. Chem. 33 (1994) 5065-5072.
- [57] M.T. Green, J.H. Dawson, H.B. Gray, Science 304 (2004) 1653-1656.
- [58] T.H. Chen, N. Asiri, K.W. Kwong, J. Malone, R. Zhang, Chem. Commun. 51 (2015) 9949-9952
- [59] K.W. Kwong, D. Patel, J. Malone, N.F. Lee, B. Kash, R. Zhang, New J. Chem. 41 (2017) 14334-14341.
- [60] N.-F. Lee, D. Patel, H.Y. Liu, R. Zhang, J. Inorg. Biochem. 183 (2018) 56-65.
- [61] Z. Pan, R. Zhang, L.W.M. Fung, M. Newcomb, Inorg. Chem. 46 (2007) 1517–1519.
- [62] Z. Pan, M. Newcomb, Inorg. Chem. Commun. 14 (2011) 968-970.
- [63] K. Nishikawa, Y. Honda, H. Fujii, J. Am. Chem. Soc. 142 (11) (2020) 4980-4984.
- [64] T.G. Traylor, F. Xu, J. Am. Chem. Soc. 112 (1990) 178-186.
- [65] T.C. Bruice, Acc. Chem. Res. 24 (1991) 243-249.
- [66] W. Nam, H.J. Han, S.-Y. Oh, Y.J. Lee, M.-H. Choi, S.-Y. Han, C. Kim, S.K. Woo, W. Shin, J. Am. Chem. Soc. 122 (2000) 8677-8684.
- [67] S. Yokota, H. Fujii, J. Am. Chem. Soc. 140 (2018) 5127-5137.
- [68] A.S. Faponle, M.G. Quesne, C.V. Sastri, F. Banse, S.P. de Visser, Chem. Eur. J. 21 (2015) 1221-1236.
- [69] A. Dey, A. Ghosh, J. Am. Chem. Soc. 124 (2002) 3206-3207.
- [70] I. Wasbotten, A. Ghosh, Inorg. Chem. 45 (2006) 4910-4913.
- [71] F. Tiago de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que Jr., E.L. Bominaar, E. Muenck, T.J. Collins, Science 315 (2007) 835-838.
- S. Gupta, J. Am. Chem. Soc. 136 (2014) 9524-9527.
- [73] A.J. McGown, W.D. Kerber, H. Fujii, D.P. Goldberg, J. Am. Chem. Soc. 131 (2009) 8040-8048.
- [74] K. Cho, P. Leeladee, A.J. McGown, S. DeBeer, D.P. Goldberg, J. Am. Chem. Soc. 134 (2012) 7392–7399.
- [75] R. Zhang, D.N. Harischandra, M. Newcomb, Chem. Eur. J. 11 (2005) 5713-5720.
- [76] J.T. Groves, J. Lee, S.S. Marla, J. Am. Chem. Soc. 119 (1997) 6269-6273.
- [77] N. Jin, J.T. Groves, J. Am. Chem. Soc. 121 (1999) 2923-2924.
- [78] W. Nam, I. Kim, M.H. Lim, H.J. Choi, J.S. Lee, H.G. Jang, Chem. Eur. J. 8 (2002) 2067-2071.
- [79] J.T.K. Groves, J. William Jr., C. Haushalter Robert, J. Am. Chem. Soc. 102 (1980) 6375-6377.
- [80] C.L. Hill, B.C. Schardt, J. Am. Chem. Soc. 102 (1980) 6374–6375.
- [81] W. Liu, J.T. Groves, Acc. Chem. Res. 48 (2015) 1727-1735.
- [82] V.K. Yachandra, K. Sauer, M.P. Klein, Chem. Rev. 96 (1996) 2927–2950. [83] N. Jin, M. Ibrahim, T.G. Spiro, J.T. Groves, J. Am. Chem. Soc. 129 (2007)
- 12416-12417.
- [84] M. Schappacher, R. Weiss, Inorg. Chem. 26 (1987) 1189-1190.
- [85] R.S. Czernuszewicz, Y.O. Su, M.K. Stern, K.A. Macor, D. Kim, J.T. Groves, T.G. Spiro, J. Am. Chem. Soc. 110 (1988) 4158-4165.
- [86] K. Ayougou, E. Bill, J.M. Charnick, C.D. Garner, D. Mandon, A.X. Trautwein, R. Weiss, H. Winkler, Angew. Chem. Int. Ed. Engl. 34 (1995) 343-346.
- [87] S. Fukuzumi, N. Fujioka, H. Kotani, K. Ohkubo, Y.-M. Lee, W. Nam, J. Am. Chem. Soc. 131 (2009) 17127-17134
- [88] M. Guo, M.S. Seo, Y.-M. Lee, S. Fukuzumi, W. Nam, J. Am. Chem. Soc. 141 (2019) 12187-12191.
- [89] C.-C. Guo, H.-P. Li, J.-B. Xu, J. Catal. 185 (1999) 345-351.
- [90] K.W. Kwong, C.M. Winchester, R. Zhang, Inorg. Chim. Acta 451 (2016) 202-206.
- [91] M. Hoshino, Y. Nagashima, H. Seki, M.D. Leo, P.C. Ford, Inorg. Chem. 37 (1998) 2464-2469.
- [92] S. Klaine, F. Bratcher, C.M. Winchester, R. Zhang, J. Inorg. Biochem. 204 (2020) 110986
- [93] K.W. Kwong, T.H. Chen, W. Luo, H. Jeddi, R. Zhang, Inorg. Chim. Acta 430 (2015) 176-183.

- [94] D. Dolphin, T.G. Traylor, L.Y. Xie, Acc. Chem. Res. 30 (1997) 251-259.
- [95] Y. Huang, E. Vanover, R. Zhang, Chem. Commun. 46 (2010) 3776-3778.
- [96] J.T. Groves, R. Quinn, Inorg. Chem. 23 (1984) 3844-3846.
- [97] W.H. Leung, C.M. Che, J. Am. Chem. Soc. 111 (1989) 8812-8818.
- R. Zhang, Y. Huang, C. Abebrese, H. Thompson, E. Vanover, C. Webb, Inorg. Chim. [98] Acta 372 (2011) 152-157.
- C. Abebrese, Y. Huang, A. Pan, Z. Yuan, R. Zhang, J. Inorg. Biochem. 105 (2011) [99] 1555-1561.
- C.-M. Che, J.-L. Zhang, R. Zhang, J.-S. Huang, T.-S. Lai, W.-M. Tsui, X.-G. Zhou, Z.-[100] Y. Zhou, N. Zhu, C.K. Chang, Chem. Eur. J. 11 (2005) 7040-7053.
- [101] Z. Gross, S. Ini, Inorg. Chem. 38 (1999) 1446-1449.
- [102] J.T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, J. Am. Chem. Soc. 118 (1996) 8961-8962.
- [103] C. Wang, K.V. Shalyaev, M. Bonchio, T. Carofiglio, J.T. Groves, Inorg. Chem. 45 (2006) 4769-4782.
- [104] Z. Gross, S. Ini, J. Org. Chem. 62 (1997) 5514-5521.
- [105] H. Ohtake, T. Higuchi, M. Hirobe, Heterocycles 40 (1995) 867-903.
- [106] R. Zhang, W.-Y. Yu, K.-Y. Wong, C.-M. Che, J. Org. Chem. 66 (2001) 8145-8153.
- [107] F. Ogliaro, S.P. de Visser, J.T. Groves, S. Shaik, Angew. Chem. Int. Ed. 40 (2001) 2874-2878.
- [108] K.P. Shing, B. Cao, Y. Liu, H.K. Lee, M.-D. Li, D.L. Phillips, X.-Y. Chang, C.-M. Che, J. Am. Chem. Soc. 140 (2018) 7032-7042.
- [109] E. Vanover, Y. Huang, L. Xu, M. Newcomb, R. Zhang, Org. Lett. 12 (2010) 2246-2249
- [110] R. Zhang, E. Vanover, W.-L. Luo, M. Newcomb, Dalton Trans. 43 (2014) 8749-8756.
- [111] G. Golubkov, J. Bendix, H.B. Gray, A. Mahammed, I. Goldberg, A.J. DiBilio, Z. Gross, Angew. Chem. Int. Ed. 40 (2001) 2132-2134.
- [112] A. Kumar, I. Goldberg, M. Botoshansky, Y. Buchman, G. Z, J. Am. Chem. Soc. 132 (2010) 15233-15245.
- [113] K.W. Kwong, N.F. Lee, D. Ranburg, J. Malone, R. Zhang, J. Inorg. Biochem. 163 (2016) 39-44.
- [114] N.F. Lee, J. Malone, H. Jeddi, K.W. Kwong, R. Zhang, Inorg. Chem. Commun. 82 (2017) 27-30.
- [115] Z. Gross, G. Golubkov, L. Simkhovich, Angew. Chem. Int. Ed. Engl. 39 (2000) 4045-4047.
- [116] E.G. Samsel, K. Srinivasan, J.K. Kochi, J. Am. Chem. Soc. 107 (1985) 7606–7617.
- [117] K. Srinivasan, P. Michand, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309–2320.
- [118] F.N. Jacobsen, G.W. Wilkinson, F.G.A. Stone, F.W. Abel, L.S. Hegedus (Eds.). Comprehensive Organometallic Chemistry II, Pergamon, New York, 1995, p. 1097.
- [119] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189-214.
- [120] T. Katsuki, Synlett (2003) 281-297.
- [121] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801-2803.
- [122] R. Irie, K. Noda, Y. Ito, T. Katsuki, Tetrahedron Lett. 32 (1991) 1055–1058.
- [123] S. Klaine, N.F. Lee, A. Dames, R. Zhang, Inorg. Chim. Acta 509 (2020) 119681.
- [124] T.H. Chen, K.W. Kwong, N.G. Lee, D. Ranburger, R. Zhang, Inorg. Chem. Acta 451 (2016) 65-72
- [125] D. Ranburger, B. Willis, B. Kash, H. Jeddi, C. Alcantar, R. Zhang, Inorg. Chim. Acta 487 (2019) 41-49.
- [126] S.H. Wang, B.S. Mandimutsira, R. Todd, B. Ramdhanie, J.P. Fox, D.P. Goldberg, J. Am. Chem. Soc. 126 (2004) 18-19.
- [127] D.N. Harischandra, G. Lowery, R. Zhang, M. Newcomb, Org. Lett. 11 (2009) 2089-2092
- [128] R. Zhang, E. Vanover, T.-H. Chen, H. Thompson, Appl. Catal. A 465 (2013) 95-100
- [129] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, Chem. Eur. J. 7 (2001) 1041-1055.
- [130] J.P. Collman, C.E. Barnes, P.J. Brothers, T.J. Collins, T. Ozawa, J.C. Gallucci, J.A. Ibers, J. Am. Chem. Soc. 106 (1984) 5151-5163.
- [131] H. Sugimoto, T. Higashi, M. Mori, M. Nagano, Z. Yoshida, H. Ogoshi, Bull. Chem. Soc. Jpn. 55 (1982) 822-828.
- [132] J.-L. Zhang, C.-M. Che, Chem. Eur. J. 11 (2005) 3899-3914.
- [133] N.-H. Tran, D. Nguyen, S. Dwaraknath, S. Mahadevan, G. Chavez, A. Nguyen, T. Dao, S. Mullen, T.-A. Nguyen, L.E. Cheruzel, J. Am. Chem. Soc. (2013) 14484-14487.

[72] M. Ghosh, K.K. Singh, C. Panda, A. Weitz, M.P. Hendrich, T.J. Collins, B.B. Dhar,