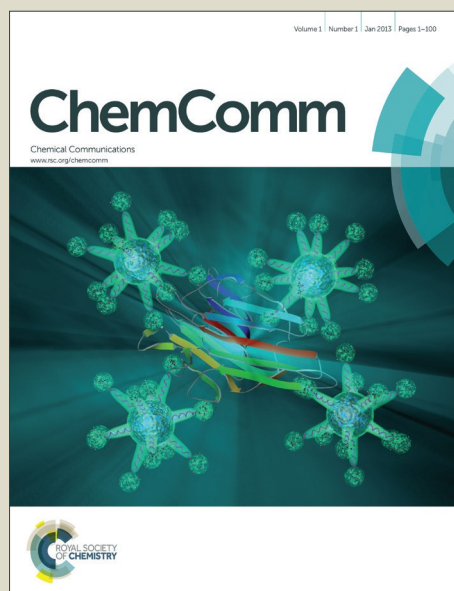


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## Ligand control in photochemical generation of high-valent porphyrin-iron-oxo derivatives

Tse-Hong Chen,<sup>a</sup> Nawras Asiri,<sup>a</sup> Ka Wai Kwong,<sup>a</sup> Jonathan Malone<sup>a</sup> and Rui Zhang<sup>\*a</sup>Received 00th January 20xx,  
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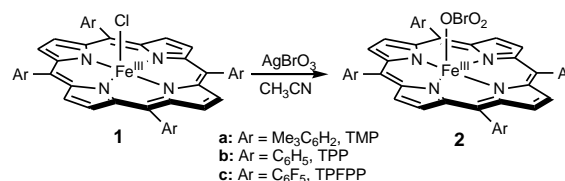
**Visible-light irradiation of photo-labile bromate porphyrin-iron(III) salts gave iron(IV)-oxo porphyrin radical cations (compound I model) or the neutral iron(IV)-oxo porphyrin (compound II model), depending on the electronic structure of porphyrin ligands.**

High-valent iron-oxo intermediates play central roles as active oxidants in enzymatic and synthetic catalytic oxidations.<sup>1-3</sup> In particular, the iron(IV)-oxo porphyrin radical cations, which have been known for decades, are observed intermediates in peroxidase and catalase enzymes (biologically termed as compound I) and synthetic models.<sup>4-6</sup> A compound I species is also thought to be the oxidizing transient in the cytochrome P450 enzymes,<sup>7, 8</sup> and recent advance provided the spectroscopic and kinetic characterization of the long-sought intermediate.<sup>9</sup> In general, iron(IV)-oxo neutral porphyrins, so-called compound II, are relatively stable, and therefore, less reactive in oxo-transfer reactions in comparison to compound I.<sup>4, 5, 10, 11</sup> True iron(V)-oxo complexes are generally rare and elusive, and considered to be more reactive than the iron(IV)-oxo ligand radical cations.<sup>12</sup> For examples, the putative porphyrin/corrole-iron(V)-oxo transients produced by laser flash photolysis (LFP) methods displayed an appropriate high level of reactivity.<sup>13-15</sup> In the Rieske dioxygenase enzymes and their synthetic functional models, non-heme iron(V)-oxo intermediates have been reported to be the reactive intermediates in hydroxylation and epoxidation reactions.<sup>16, 17</sup> The spectroscopic evidence for a high-valent corrolazine-iron-oxo intermediate at the iron(V) oxidation level has also been reported.<sup>18, 19</sup>

Compound I model complexes produced by oxidations of porphyrin-iron(III) salts with oxidants such as *m*CPBA or ozone,<sup>20-22</sup> have been characterized by various spectroscopic methods.<sup>23</sup> As an alternative to two-electron chemical oxidations of iron(III) porphyrins, photochemical oxidations of iron(IV)-oxo neutral porphyrins to generated compound I species in enzymes and in models were also reported.<sup>24, 25</sup> Notably, the photochemical approach produces metal-oxo species essentially instantly, and permits direct

detection of metal-oxo species and kinetic studies of their oxidations within much shorter timescales than the fastest mixing experiments.<sup>13, 14, 26, 27</sup> In this regard, the photo-induced ligand cleavages reactions have been developed to generate a variety of high-valent metal-oxo species in porphyrin and corrole systems.<sup>28</sup> In addition, we extended photo-induced ligand cleavage reactions to generate *trans*-dioxoruthenium(VI) porphyrins in sterically bulky and non-bulky porphyrins<sup>29, 30</sup> and a highly reactive ruthenium-oxo species<sup>31</sup> that also found in a photo-disproportionation of the *bis*-porphyrin-ruthenium(IV)  $\mu$ -oxo dimer.<sup>32</sup> In this work, we report a new photochemical entry to compound I and II model complexes, depending on the electronic nature of porphyrin ligands.

The three systems studied in this work are shown in Scheme 1. 5,10,15,20-tetramesitylporphyrin-iron(III) chloride, (TMP)Fe<sup>III</sup>(Cl) (**1a**), 5,10,15,20-tetraphenylporphyrin-iron(III) chloride, (TPP)Fe<sup>III</sup>(Cl) (**1b**), and 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin-iron(III) chloride, (TPFPP)Fe<sup>III</sup>(Cl) (**1c**), are known compounds. Facile exchange of the counterions in **1** with excess amount of Ag(BrO<sub>3</sub>) gave the corresponding bromate salts **2**, and their formation was indicated by the UV-vis spectra. These species **2** were photo-labile and subsequently used for photochemical reactions.



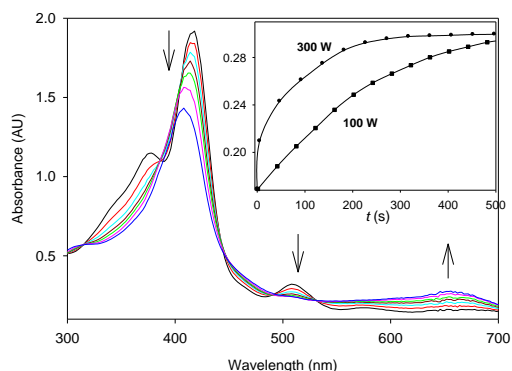
### Scheme 1

Irradiation of bromate complex **2a** in anaerobic CH<sub>3</sub>CN with visible light from a tungsten lamp (100 W) resulted in change in absorption spectra with isosbestic points at 528, 488, 446, 384 and 342 nm (Fig. 1). Over a time period of 9 min, **2a** was decayed, and *greenish* species **3a** was produced, displaying a weaker Soret band at 404 nm and stronger Q band at 656 nm that are characteristic for iron(IV)-oxo porphyrin radical cations.<sup>20</sup> Accordingly, **3a** was assigned as Fe<sup>IV</sup>(O)(TMP<sup>+</sup>) on the basis of its distinct UV-vis absorption and reactivity discussed below. The spectra signature of Fe<sup>IV</sup>(O)(TMP<sup>+</sup>) was further confirmed by production of the same species in the mixing chemical oxidation of **1a** with *m*CPBA (see Fig. S1 in supporting information). Control experiments showed that no

<sup>a</sup> Department of Chemistry, Western Kentucky University, 1906 College Heights Blvd., Bowling Green, Kentucky, USA. Fax: 1-270-7455631; Tel: +1-270-7453803; E-mail: [rui.zhang@wku.edu](mailto:rui.zhang@wku.edu)

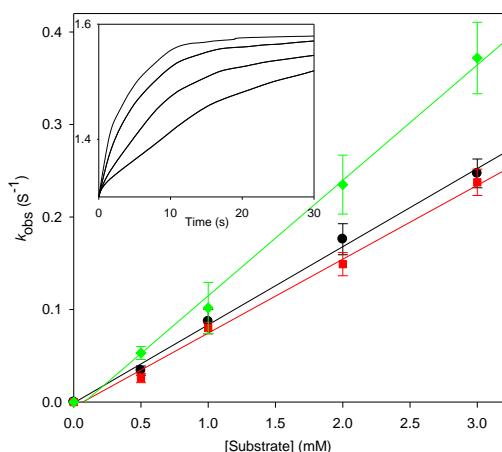
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

species **3a** was formed in the absence of light. In a series of reactions, the transformation of **2a** to **3a** was more rapidly at higher power of visible light (see Inset in Fig. 1).



**Fig. 1** Time-resolved spectra of **3a** ( $1.0 \times 10^{-5}$  M) following irradiation of **2a** with visible light (100 W) in anaerobic  $\text{CH}_3\text{CN}$  solution at 23 °C. Spectra were recorded at  $t = 0, 1, 2, 3, 5, 7$  and 9 min. Inset is kinetic traces monitored at 656 nm with different power of lights.

In a preparative reaction, the photo-generated **3a** was found to react as a competent oxo-transfer agent with various two-electron reductants such as *cis*-cyclooctene.<sup>33</sup> In the presence of organic substrate, the time-resolved spectrum shows the clean conversion of **3a** to regenerate the iron(III) species with a  $\lambda_{\text{max}}$  of 416 nm (see Fig. S2 in supporting information). In kinetic studies, we monitored the absorbance in the Soret band region at 416 nm, which increased over the course of reaction because the absorbance for the iron(III) salt is stronger than the oxo **3a** (Inset in Fig. 2). The traces were fit to single-exponential decay, as expected for reactions under pseudo-first-order conditions. Plots of  $k_{\text{obs}}$  versus [Sub] typically gave straight lines with near-zero intercepts; examples are shown in Fig. 2. We measured the kinetics in four sets of studies for several substrates with three independent kinetic runs, and the second-order rate constants are listed in Table 1, comparable with the literature reported  $k_{\text{ox}}$  for oxidant **3a** produced from chemical oxidation by *m*CPBA.<sup>34</sup>



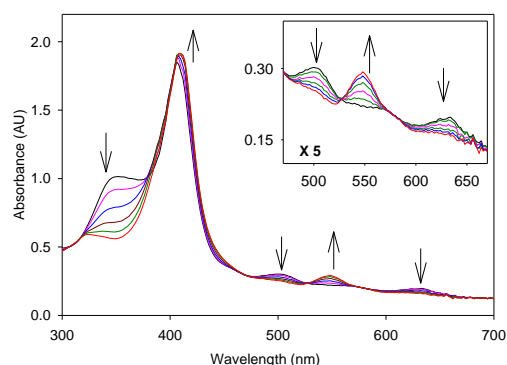
**Fig. 2** Kinetic plots of the observed rate constants versus the concentration of representative substrates: *cis*-stilbene (◆), cyclohexene (●) and *cis*-cyclooctene (■). Inset showing traces at 416 nm for reactions of **3a** with *cis*-cyclooctene at 3.0, 2.0, 1.0 and 0.5 mM concentrations.

**Table 1.** Second-order rate constants for reactions of porphyrin-iron(IV)-oxo species<sup>a</sup>

Substrate	Rate constant ( $\text{M}^{-1} \text{s}^{-1}$ )		
	<b>3a</b> <sup>b</sup>	<b>3a</b> <sup>c</sup>	<b>3c</b> <sup>d</sup>
<i>cis</i> -cyclooctene	$79 \pm 3$	$62 \pm 2$	$(1.8 \pm 0.1) \times 10^{-2}$
cyclohexene	$85 \pm 6$	$68 \pm 3$	$(6.0 \pm 0.1) \times 10^{-2}$
<i>cis</i> -stilbene	$120 \pm 9$	$90 \pm 2$	$(2.1 \pm 0.1) \times 10^{-2}$
ethylbenzene	$1.0 \pm 0.1$	$0.9 \pm 0.1$ <sup>b</sup>	-

<sup>a</sup> In  $\text{CH}_3\text{CN}$  at  $23 \pm 2$  °C. The values are average of 2-3 runs with 2 standard deviation; <sup>b</sup> Photo-generated from this work. <sup>c</sup> Formed by *m*CPBA oxidation in ref. 34. <sup>d</sup> Obtained from results in ref. 36

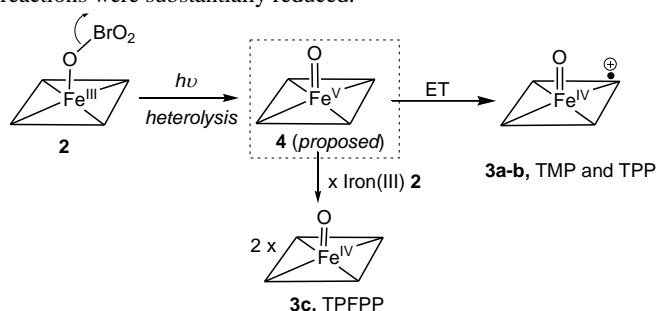
In a fashion similar to that described for the generation of **3a**, the sterically unhindered  $\text{Fe}^{\text{IV}}(\text{O})(\text{TPP}^+)$  (**3b**) was also formed, decaying slightly faster than **3a** in a self-decay reaction (Fig. S3 in supporting information). In contrast, visible-light irradiation of bromate complex **2c** with a highly electron-deficient porphyrin (TPFPP) gave distinctly different species than those produced by photolyses of complexes **2a-b**. Fig. 3 shows the time-resolved spectra for generating a red species **3c**. We characterized **3c** as porphyrin-iron(IV)-oxo derivative, and the process at  $\lambda = 410$  and 548 nm were identical those for  $\text{Fe}^{\text{IV}}(\text{O})(\text{TPFPP})$ .<sup>35</sup> Apparent second-order rate constants determined from pseudo-first-order kinetic studies for reactions of **3c** with alkenes are about 2 to 3 orders of magnitude smaller in comparison with those of species **3a** and **b** with same reductants (Table 1).<sup>36</sup>



**Fig. 3** Time-resolved spectra of **3c** ( $1.0 \times 10^{-5}$  M) following irradiation of **2c** with visible light (100 W) over 20 min in anaerobic  $\text{CH}_3\text{CN}$  solution at 23 °C.

Photolysis of (porph) $\text{Mn}^{\text{III}}(\text{ClO}_4)$  complexes was previously reported to give (porph) $\text{Mn}^{\text{V}}(\text{O})$  species by heterolytic cleavage of the O-Cl bond.<sup>27</sup> Recent studies showed that heme iron(III)-hydroperoxy complexes thermodynamically led via heterolytic O-O bond cleavage to a high-valent iron(IV)-oxo heme cation radical intermediate.<sup>37</sup> Thus, the photolysis reactions of the bromate complexes **2** may undergo the similar *heterolytic* cleavage of the O-Br bond in the bromate counterions that results in a two-electron photo oxidation (Scheme 2).<sup>28</sup> In this way, one can logically speculate that the first-formed intermediate could be a porphyrin-iron(V)-oxo species which is proposed to be a higher-energy isoelectronic isomer<sup>23</sup> than an iron(IV)-oxo porphyrin radical cation. In porphyrin and corrole complexes, computational results<sup>12, 38</sup> indicate that some iron(V)-oxo species should be experimentally accessible. Much evidence has accumulated in recent reports that putative iron(V)-oxo intermediates can be involved in photochemical oxy-ligand fragmentation reaction, although their identities are needed to be characterized more fully.<sup>13-15</sup> As thermodynamically favored, iron(V)-oxo species **4** might react to compound I by internal electron transfer (ET) from the porphyrin

to the iron (Scheme 2). In the TPFPP system, the ET from the highly electron-deficient porphyrin to the iron sequence is apparently not favored in view of a high redox potential or energy barrier, and the interesting possibility exists that the observed iron(IV)-oxo derivative (**3c**) might be formed by comproportionation reactions of **4** with the residual iron(III) products. Previous studies with manganese-oxo species found that porphyrin-manganese(V)-oxo species comproportionate rapidly with manganese(III) species,<sup>27</sup> and corrole-manganese(V)-oxo species reacted with corrole manganese(III) species to give manganese(IV) species.<sup>39</sup> However, the comproportionation reactions between porphyrin-iron(IV)-oxo radical cations and iron(III) salts were much too slow to be important.<sup>34</sup> The distinction between the two possibilities will be determined by the electronic structure or redox potential of porphyrin ligand, if any, for electron spin distribution of atomic orbitals and bond reorganizations needed to form the two species.<sup>23</sup> In addition, we found that irradiation of chlorate complexes **2** also gave oxo radical cations **3a-b** or neutral iron(IV)-oxo **3c** similar to that of bromate precursors, but the rates and efficiencies of the photolysis reactions were substantially reduced.



**Scheme 2.** Mechanistic considerations on photochemical formation of iron(IV)-oxo porphyrin radical cations and iron(IV)-oxo neutral porphyrin controlled by porphyrin ligands. The parallelogram represents a porphyrin.

In summary, we report here a new photochemical entry to access high-valent iron-oxo model derivatives. As controlled by the electronic nature of porphyrin ligands, iron(IV)-oxo porphyrin radical cations and iron(IV)-oxo porphyrin derivatives were produced, respectively, by visible light irradiation of the corresponding iron(III) bromate complexes. These observations indicate that the photochemical reactions involve a heterolytic cleavage of O-Br in precursors **2** to give a putative iron(V)-oxo intermediate, which might relax to compound I through electron transfer from porphyrin to the iron or undergo rapid comproportionation reaction with residual iron(III) to afford compound II derivative. We believe this work will stimulate the further exploration of photo-synthetic methodology to produce and study other high-valent metal-oxo complexes.

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## Notes and references

§ Electronic Supplementary Information (ESI) available: [UV-vis spectra of **3a** produced by chemical method, and time-resolved spectra for reaction of **3a** with *cis*-cyclooctene, and time-resolved spectra for generating **3b**]. See DOI: 10.1039/b000000x/

§§ Abbreviations used in this study: TMP = 5,10,15,20-tetra mesitylporphyrin (**a**); TPP = 5,10,15,20-tetraphenylporphyrin (**b**);

TPFPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**c**); mCPBA = *meta*-chloroperoxybenzoic acid. All commercial reagents including **1c** were of the best available purity and were used as supplied unless otherwise specified. HPLC grade acetonitrile (99.93%) was distilled over P<sub>2</sub>O<sub>5</sub> prior to use. 5,10,15,20-Tetramesitylporphyrin (TMPH<sub>2</sub>), tetraphenylporphyrin (TPPH<sub>2</sub>)<sup>41</sup> free ligands and their iron(III) chlorate complexes Fe<sup>III</sup>(Por)Cl (**1a** and **1b**) were prepared by literature methods.<sup>42</sup> Treatment of compounds **1** (typically 5 mg) with *ca.* 10-fold excess of Ag(BrO<sub>3</sub>) in anaerobic CH<sub>3</sub>CN gave the bromate complexes **2**, monitored by UV-vis. When the solution of **2** with concentration in the range of (6–12) × 10<sup>-6</sup> M was irradiated with visible light from a tungsten lamp (60 and 300 W) at ambient temperature, the formation of **3** was complete in *ca.* 5–20 min, monitored by UV-visible spectroscopy. These species **2** were photolabile, prepared *in situ*, and subsequently used for photochemical reactions (*Caution! Bromate salts of metal complexes are potentially explosive and should be handled with care*). Reactions of oxo-species **3a** with excess of organic substrates (> 100 equiv.) were conducted in an acetonitrile solution at 23 ± 2 °C. The rates of the oxo group transfer reactions from **3a** to alkene were monitored by the decay of the Soret absorption band of the oxo-species **3a**. The kinetic traces at λ<sub>max</sub> of Soret band displayed good pseudo-first-order behavior for at least 10 half-lives, and the data gave pseudo-first-order observed rate constants, *k*<sub>obs</sub>. Plots of these values against the concentration of substrate (final concentration) were linear and the slope gave the second-order rate constant, which is average of 2–3 determination, consisting of 4 independent kinetic measurements.

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33. **3a** was prepared by mixing **1a** with ca. 1.5 equiv. of Ag(BrO<sub>3</sub>) in anaerobic CH<sub>3</sub>CN under visible light irradiation; the estimated yield of **3a** determined by UV-visible spectroscopy was > 95%. An large excess of *cis*-cyclooctene (> 100 equiv.) was added, and the mixture was stirred for 10 min at ambient conditions. Following product workup, quantitative GC analysis showed the presence of *cis*-cyclooctene oxide in > 90% yield based on precursor **1a**.
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