

Substrate oxidation by an iron(IV)-oxo complex bearing a porphyrin derivative as the ancillary ligand having a substrate-trapping site

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As seen in the picket-fence porphyrins,¹ building steric structures around porphyrin peripheries is a common method to investigate the second-coordination-sphere effects on the reactivity of metalloporphyrins. In our group, selective convergence to each atropisomer from an isomeric mixture of a TPP derivative (**1**), having *meso*-aryl groups substituted with mesityl groups at one of the *o*-positions, has been successfully achieved by simple procedures such as heating.² The $\alpha\alpha\alpha\alpha$ isomer of **1** was obtained in 60% isolated yield by heating in CHCl₃ at 60 °C.² Herein, we have used an iron complex of the $\alpha\alpha\alpha\alpha$ isomer of **1** ($\alpha\alpha\alpha\alpha$ -**1**) to reveal effects of the hydrophobic cavity formed by the *o*-substituents of the *meso*-aryl groups on the substrate oxidation.

An Fe^{III} ion was inserted into the center of $\alpha\alpha\alpha\alpha$ -**1** to obtain an Fe^{III} complex, $\alpha\alpha\alpha\alpha$ -Fe^{III}-**1** and its structure was revealed by X-ray diffraction analysis (Figure 1a). After removing the axial Cl ligand, $\alpha\alpha\alpha\alpha$ -Fe^{III}-**1** was treated with *m*CPBA (= *m*-chloroperoxybenzoic acid) to obtain $\alpha\alpha\alpha\alpha$ -Fe^{IV}(O)(**1**⁺), which is a

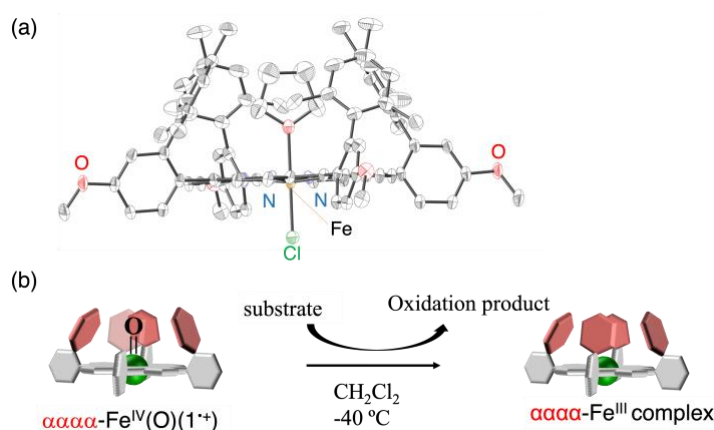


Figure 1. (a) Crystal structure of $\alpha\alpha\alpha\alpha$ -Fe^{III}-**1** from the side view, (b) substrate oxidation by $\alpha\alpha\alpha\alpha$ -Fe^{IV}(O)(**1**⁺).

derivative of so-called “compound I”. $\alpha\alpha\alpha\alpha$ -Fe^{IV}(O)(**1**⁺) was characterized by ESR and UV-Vis spectroscopies. The kinetic studies for the substrate oxidation by $\alpha\alpha\alpha\alpha$ -Fe^{IV}(O)(**1**⁺) revealed that the substrate oxidation included a pre-equilibrium process, in which the substrate was captured around the iron-oxo site. Herein, we will report the details of the substrate oxidation by $\alpha\alpha\alpha\alpha$ -Fe^{IV}(O)(**1**⁺).

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