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## **Graphical Abstract**

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Binuclear iron(III) perfluoro(tetraazaporphyrin) µ-Leave this area blank for abstract info. oxodimer: a highly efficient catalyst for biomimetic oxygenation reactions Mekhman S. Yusubov\*, Cumali Celik, Margarita R. Geraskina, Akira Yoshimura, Viktor V. Zhdankin\* and Victor N. Nemykin\* Bu Oxone, catalyst (0.5 mol% MeCN/H<sub>2</sub>O, rt, 5 min (PhO)<sub>n</sub>, catalyst (5 mol%) PhCH<sub>3</sub> CH<sub>2</sub>Cl<sub>2</sub>, rt, 30 min MA 

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# Binuclear iron(III) octakis(perfluorophenyl)tetraazaporphyrin $\mu$ -oxodimer: a highly efficient catalyst for biomimetic oxygenation reactions

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ABSTRACT

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*Keywords:* oxygenation catalytic oxidation phthalocyanines tetraazaporphyrin Binuclear iron(III) octakis(perfluorophenyl)tetraazaporphyrin  $\mu$ -oxodimer complex was prepared by the reaction of bis(perfluorophenyl)maleonitrile and Fe(CO)<sub>5</sub> and tested in catalytic oxygenation reactions of several hydrocarbons in comparison with the analogous non-fluorinated phthalocyanine complexes. Results of the study demonstrate that this complex is a highly efficient catalyst for oxygenation of anthracene, 2-*tert*-butylanthracene, naphthalene, 2-methylnaphthalene, phenanthrene, adamantane, and toluene using iodosylbenzene, oligomeric iodosylbenzene sulfate, or Oxone as stoichiometric oxidants.

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Transition-metal porphyrins, phthalocyanines, and related compounds are widely used as catalysts in the reactions mimicking natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes.<sup>1</sup> It has also been demonstrated that porphyrin and phthalocyanine iron  $\mu$ -oxo-,<sup>2a-c</sup> and  $\mu$ -nitridodimers,<sup>2d-f</sup> which were earlier considered as catalytically inactive compounds, have high catalytic activity in different oxidation reactions. In particular, iron phthalocyanine-( $\mu$ -oxodimer) complexes have been found to be active catalysts in biomimetic oxygenations of aromatic hydrocarbons using iodosylbenzene, 2-iodylbenzoate ester, and oligomeric iodosylbenzene sulfate (PhIO)<sub>3</sub>SO<sub>3</sub>, as terminal oxidants.<sup>4</sup>

In spite of the high catalytic activity, synthetic application of iron(III) phthalocyanine( $\mu$ -oxodimer)complexes is limited due to their low stability toward oxidative degradation under reaction conditions. It is known that the introduction of fluorine atoms into the molecule significantly increase stability of the porphyrin moiety; for example, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin is a well known,

commercially available catalyst which has a relatively high resistance toward oxidative degradation. However, the resistance of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin toward oxidative degradation is limited due to the presence of C–H bonds in the four pyrrole units of the porphyrine ring. In present communication, we describe the preparation and catalytic activity of the first example of a transition-metal fully fluorinated tetraazaporphyrin complex, the binuclear iron(III) octakis-(perfluorophenyl)tetraazaporphyrin  $\mu$ -oxodimer 1 (Figure 1), which does not have any C–H bonds in its structure and exhibits an exceptional resistance to oxidative degradation.

Complex 1 was synthesized using direct high-temperature reaction between bis(perfluorophenyl)maleonitrile and  $Fe(CO)_5$  (see experimental details in Supplementary Material).

Catalytic activity of perfluoro(tetraazaporphyrin) complex 1 towards oxygenations of aromatic hydrocarbons was investigated in comparison with the analogous non-fluorinated phthalocyanine complexes 2 and  $3.^{2ac,4}$ . The results of catalytic oxidations of anthracene 4, 2-*tert*-butylanthracene 7, naphthalene 9, 2-methylnaphthalene 11, phenanthrene 16, adamantane 18 and

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toluene using iodosylbenzene or oligomeric iodosylbenzene sulfate<sup>5</sup> as sources of oxygen and catalyst 1 are summarized in Table 1.

At first, a set of preliminary experiments was performed to test the appropriate amount of catalyst needed for efficient oxygenation of anthracene, which is the most commonly used aromatic substrate for catalytic oxygenations (Table 1, entries 1-3). The oxidation of anthracene 4 was carried out in dry dichloromethane with complex 1 and PhIO (10 equiv) under stirring at room temperature. Samples of the reaction mixture were collected at every 5 minutes, filtered through silica gel, washed with a mixture of ethyl acetate and hexanes (2:3, v:v), and analyzed by GC-MS. This study has demonstrated that the oxygenation of anthracene with a 100% conversion to anthraquinone 5 was observed when 2 mol% of catalyst 1 was used with full conversion of the substrate in 2 hours (entry 3). For comparison, 10 mol% of catalyst is required for a similar oxygenation using phthalocyanine-(µ-oxodimer) complexes 2 and 3 (entries 4 and 5).



Figure 1. Binuclear iron(III) perfluoro(tetraazaporphyrin) µ-oxodimer 1.



Figure 2. Iron(III) phthalocyanine-( $\mu$ -oxodimer) complexes 2 and 3.

The complete conversion of a less reactive substrate, 2-*tert*butylanthracene **6**, to give product **7** was reached in 1 hour in CH<sub>2</sub>Cl<sub>2</sub> using catalyst **1** (5 mol%) and PhIO or in 6 min with catalyst **1** (1 mol%) and oligomeric iodosylbenzene sulfate, (PhIO)<sub>3</sub>SO<sub>3</sub>, as the more reactive source of oxygen (entries 6 and 7). A similar oxygenation with catalyst **2** (15 mol%) and PhIO requires 20 hours at room temperature (entry 8).<sup>4c</sup> Likewise, the oxygenation of naphthalene **8** and 2-methylnaphthalene **10** with the catalyst **1**/PhIO system proceeds very fast with the low catalyst loading of 1-2 mol%, which is much more efficient compared to catalyst **2** (entries 9-11). The oxidation of 2methylnaphthalene **10** gives a mixture of products **11** and **12**, which is in agreement with the previously reported oxygenations of this substrate.<sup>2.6</sup>

Even more impressive results were obtained in the oxygenation of the least reactive aromatic substrate, phenanthrene 13, to give product 14 (entries 12 and 13). A complete oxygenation of phenanthrene with 2 mol% of catalyst 1 occurs in 2 hours, while no reaction is observed in the presence of catalyst 2 (15 mol%).

In contrast with the non-fluorinated catalysts 2 and 3, iron(III) octakis(perfluorophenyl)tetraazaporphyrin  $\mu$ -oxodimer 1 is an efficient catalyst for the oxidation of C–H bonds at sp<sup>3</sup>-hybridized carbon. When adamantane 15 was used as a substrate with 2 mol% of catalyst 1, the mixture of products 1-adamantanol 16 and 2-adamantanone 17 was obtained in high yield (entry 14). For comparison, no reaction was observed with catalyst 2 (entry 15), and only 2.4% conversion was achieved in 24 hours with catalyst 3 (15 mol%) giving 1-adamantanol as the product (entry 16).

The oxidation of toluene in the presence of catalyst 1 (5 mol%) gave a mixture of oxygenated products (mainly, quinone 18) with a 100% conversion in 30 min (entry 17). This is an impressive proof of high reactivity of catalyst 1, as toluene previously has been commonly used as a nonreactive organic solvent for similar metalloporphyrin-catalyzed oxygenation reactions (cf. entry 18).



Table 1. Catalytic activity of iron(III) octakis(perfluorophenyl)tetraazaporphyrin 1 in oxygenation reactions in comparison with phthalocyanine complexes 2 and 3.

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<sup>a</sup>Reactions were performed in dichloromethane at room temperature using iodosylbenzene (10 equiv) as source of oxygen unless otherwise noted.

<sup>b</sup>Toluene was used as solvent; data from literature.<sup>4c</sup>

<sup>c</sup>Methanol was used as solvent; data from literature.<sup>4c</sup>

<sup>d</sup>Oligomeric iodosylbenzene sulfate, (PhIO)<sub>3</sub>SO<sub>3</sub>, was used as source of oxygen.

eToluene was used as solvent and (PhIO)<sub>3</sub>SO<sub>3</sub> as source of oxygen; data from literature.<sup>4c</sup>

<sup>f</sup>The presence of several regioisomeric products of hydroxylation was also detected by GC-MS in this reaction.

<sup>g</sup>No reaction observed under these conditions in the presence of catalyst 2.4c

At the next step, we investigated oxygenations in the presence of catalyst 1 and different common oxidants (oligomeric iodosylbenzene sulfate, Oxone, peracetic acid, hydrogen peroxide) in aqueous acetonitrile using 2-tert-butylanthracene 6 as the standard substrate (Table 2). 2-tert-Butylanthracene was selected because it is oxidized relatively slow, probably due to the steric hindrance caused by the tert-butyl group, selectively producing anthraquinone 7 as a single product (Table 1, entries 6-8). The oxygenation of 2-tert-butylanthracene 6 in dry dichloromethane with catalyst 1 (1 mol%) using oligomeric iodosylbenzene sulfate gives 100% conversion in 6 minutes (entry 7). The same reaction in acetonitrile-water (1:1) mixture requires even smaller quantity of catalyst 1 (0.5 mol%) to give 100% conversion in 5 minutes (Table 2, entry 1). Oxone (2KHSO<sub>5</sub>•KHSO<sub>4</sub>•K<sub>2</sub>SO<sub>4</sub>) has about the same reactivity as oligomeric iodosylbenzene sulfate (entry 2), whereas peracetic acid and hydrogen peroxide are not efficient sources of oxygen in these reaction (entries 3 and 4).

<b>Table 2.</b> Oxygenations of 2- <i>tert</i> -butylanthracene 6 in the
presence of catalyst 1 with different oxidants. <sup>a</sup>

Entry	Oxidant	Time (min)	Conversion of 6 to 7
1	(PhIO) <sub>3</sub> SO <sub>3</sub>	5	100
2	Oxone	5	100
3	CH <sub>3</sub> CO <sub>3</sub> H/CH <sub>3</sub> CO <sub>2</sub> H	1440	44
4	30% aq H <sub>2</sub> O <sub>2</sub>	4320	0

<sup>a</sup>Reactions were performed in acetonitrile-water (1:1) at room temperature with terminal oxidant (6 equiv of active O) and 0.5 mol% of catalyst **1**.

These results demonstrate that oligomeric iodosylbenzene sulfate and Oxone are the most powerful oxidants in the iron(III) octakis(perfluorophenyl)tetraazaporphyrin-catalyzed

oxygenations. In order to further compare reactivity of these two oxidants, we measured the number of oxygenation cycles that can be performed using the same initial quantity of catalyst 1 (0.5 mol%) and adding 1 equiv of substrate **6** and excessive oxidant

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(6 equiv of active O) several times, until conversion of 6 to 7 falls below 100% and this value stays unchanged (Table 3). These data in principle allow us to compare stability of the catalyst toward oxidative degradation in the presence of different oxidants under reaction conditions.

**Table 3.** Oxygenation cycles in the reactions of 2-*tert*butylanthracene **6** with different oxidants in the presence of fixed quantity of catalyst **1** (0.5 mol%).<sup>a</sup>

Entry	Oxidant	Cycle	Time (min)	Conversion of <b>6</b> to <b>7</b>
1	(PhIO) <sub>3</sub> SO <sub>3</sub>	1 <sup>st</sup> addition	5	100
2	(PhIO) <sub>3</sub> SO <sub>3</sub>	2 <sup>nd</sup> addition	5	100
3	(PhIO) <sub>3</sub> SO <sub>3</sub>	3 <sup>rd</sup> addition	10	100
4	(PhIO) <sub>3</sub> SO <sub>3</sub>	4 <sup>th</sup> addition	20	100
5	(PhIO) <sub>3</sub> SO <sub>3</sub>	$5^{th}$ addition	20	100
6	(PhIO) <sub>3</sub> SO <sub>3</sub>	6 <sup>th</sup> addition	40	100
7	(PhIO) <sub>3</sub> SO <sub>3</sub>	7 <sup>th</sup> addition	90	100
8	(PhIO) <sub>3</sub> SO <sub>3</sub>	8 <sup>th</sup> addition	240	99
9	Oxone	1 <sup>st</sup> addition	5	100
10	Oxone	2 <sup>nd</sup> addition	30	100
11	Oxone	3 <sup>rd</sup> addition	1440	75

<sup>a</sup>Reactions were performed in acetonitrile-water (1:1) at room temperature using the same initial quantity of catalyst  $\mathbf{1}$  (0.5 mol%) and adding 1 equiv of substrate **6** and excessive oxidant (6 equiv of active O) several times, until conversion of **6** to **7** falls below 100%.

These data (Table 3) demonstrate that iron(III) octakis(perfluorophenyl)tetraazaporphyrin  $\mu$ -oxodimer 1 (0.5 mol%) can work highly efficiently up to 8 cycles in the oxidizing system 2-*tert*-butylanthracene **6** - oligomeric iodosylbenzene sulfate in acetonitrile-water (1:1) solvent system (entry 8). Oxone is a less efficient oxidant affording after the third addition only 75% conversion in 24 hours (entry 11). This experiment clearly indicates that oligomeric iodosylbenzene sulfate is at least twice more efficient oxidant than Oxone, and has a substantial advantage over Oxone in this oxidizing system.

In conclusion, we have reported the preparation and catalytic activity of binuclear iron(III) octakis(perfluorophenyl)tetraazaporphyrin  $\mu$ -oxodimer complex 1, which is the first example of a fully fluorinated transition-metal tetraazaporphyrin complex possessing an exceptional resistance to oxidative degradation. Complex 1 is a highly efficient catalyst for biomimetic oxidations of hydrocarbons using iodosylbenzene or Oxone as stoichiometric oxidants.

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#### Supplementary Material

Supplementary material (experimental procedures and UV-vis and MCD spectra for complex 1) associated with this article can be found, in the online version, at doi: .