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Oxidation of adamantane catalysed by imidazolylporphyrinatoiron(III) complexes and structural studies of 5-coordinating iron(III) porphyrin

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Abstract

Oxidation of adamantane with phenylperacetic acid was carried out in the presence of three imidazolyltriarylporphyrinatoiron(III) complexes having pentafluorophenyl, phenyl, and mesityl (2,4,6-trimethylphenyl) groups as *meso*-substituents and three corresponding tetraarylporphyrinatoiron(III) complexes. The yield of 1- and 2-adamantanols was 76% in the case of chloro-5-(1-methyl-2-imidazolyl)-10,15,20-tri(pentafluorophenyl)porphyrinatoiron(III) (ImTPFPP–Fe(III)Cl), whereas the yield was only 26% in the case of chloro-5,10,15,20-tetra(pentafluorophenyl)porphyrinatoiron(III) in the presence of 100 eq. *N*-methylimidazole. The apparent effect of the appended imidazolyl group is discussed in terms of a 5-coordinated dimer of ImTPFPP–Fe(III)Cl, which was observed in the ^{1}H and ^{19}F NMR, and UV–vis spectra.

Keywords: Iron porphyrin; Oxidation; Peroxy acid; Imidazole coordination; Supramolecule

1. Introduction

One-oxygen oxidation of inactive C–H bonds has been of great interest in both enzymatic reactions and synthetic organic chemistry [1]. Various metal catalysts have been developed for this purpose and discussed in relation to the excellent activation methods in natural systems [2]. Peroxidases and cytochrome P-450 have been investigated most extensively as one-oxygen oxidation catalysts. Mimics of their structure and function have been examined for nearly three decades, and their development has been a continuing target of active research [3]. The following two basic strategies are proposed for active catalysts: (1) A proximal imidazole group introduced in an iron porphyrin assists heterolytic O–O bond cleavage by the push effect [4]; (2) substituents of *meso*-aryl groups greatly affect the reactivity. For example, pentafluorophenyl and 2,6-dichlorophenyl groups significantly improve the turnover number of catalytic oxidation with the use of peracids and peroxide [5].

We report here a new iron(III) porphyrin catalyst **1** that has one 2-imidazolyl group and three pentafluorophenyl groups at *meso* positions (Fig. 1). Complex **1** is expected to form its dimer **2**, representing the otherwise difficult-to-obtain 5-coordinated iron(III) species. We previously reported such complementary dimers for zinc(II) [6], magnesium(II) [7], cobalt(II), and cobalt(III) imidazolylporphyrin [8], but not iron(III) porphyrin. Catalyst **1** shows good activity for oxidation of adamantane with phenylperacetic acid (PPAA) as the oxidant. We also report structural studies of 5-coordinated dimer **2** by UV–vis as well as ^{1}H and ^{19}F NMR spectroscopy in conjunction with elucidation of the structure of the active catalyst.

2. Experimental

2.1. Materials

All the commercially available chemicals were used directly unless otherwise described. 1-Methylimidazole and CH_2Cl_2 were distilled over CaH_2. Phenylperacetic acid (PPAA) was prepared according to the literature method [9]. 2,4,6-Tri-(*tert*-butyl)phenol (TBPH) was purified by recrystallization from hot

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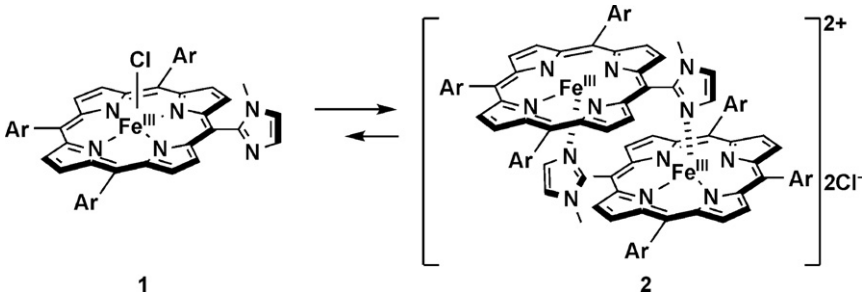

Fig. 1. Chloro(imidazolylporphyrinato)iron(III) **1** and its dimer **2**.

ethanol. Tetra(pentafluorophenyl)porphyrin [10], tetraphenylporphyrin [11], and tetra(mesityl)porphyrin [12] were prepared according to the corresponding literatures.

2.2. Instruments

^{1}H and ^{19}F NMR spectra were measured on a JEOL JNM-ECP 600 spectrometer in $CDCl_3$ or acetonitrile-d_3. ^{1}H chemical shifts were referenced to TMS as the internal standard in the case of $CDCl_3$ solution, and to the residual protons (1.96 ppm) in the case of acetonitrile-d_3 solution. ^{19}F chemical shifts were referenced to trifluoroacetic acid (−76.5 ppm) as the external standard. UV–vis spectra were measured by a Shimadzu UV-3000 PC spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer. MALDI-TOF mass spectra were measured on a Perseptive Biosystems Voyager DE-STR or Shimadzu AXIMA with dithranol as a matrix. High-resolution mass spectra (FAB method, *m*-NBA as a matrix) were measured on a JEOL *M*Station. TLC was operated on glass plates coated with 60 F_{254} (Merck) silica gel. Column chromatography was undertaken using a column packed with silica gel 60 N (Kanto Chemical, spherical, neutral, 63–210 μm). Gas chromatography was carried out on a Shimadzu GC-14B gas chromatograph with an FID detector using a 0.25 mm × 30 m dimethylpolysiloxane capillary column (DB-1, J&W Scientific).

2.3. Porphyrin synthesis

2.3.1. 5-(1-Methyl-2-imidazolyl)-10,15,20-tris(pentafluorophenyl)porphyrin, $ImTPFPPH_2$

1-Methyl-2-imidazolecarboxaldehyde (93.6 mg, 0.85 mmol, 1.0 eq.) and pentafluorobenzaldehyde (500 mg, 2.55 mmol, 3.0 eq.) were dissolved in refluxing propionic acid (50 mL). Pyrrole (228 mg, 3.40 mmol, 4.0 eq.) was then added quickly to the boiling solution. The mixture was heated under reflux for 4 h. The solvent of the reaction mixture was removed by distillation under reduced pressure. The ethyl acetate solution (100 mL) of the residue was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude material included tetraarylporphyrin, target monoimidazolylporphyrin, and other multi-imidazolylporphyrins. The residue was purified by silica gel column chromatography eluting with chloroform/acetone (10/1). The least polar tetraarylporphyrin was eluted first, and then a porphyrin mixture (82.5 mg) containing predominantly the target was followed. Since the mixture included not only the target but also many byproducts having similar polarities, the free base porphyrin was once converted to the zinc form which was less polar than the byproducts due to complementary coordination [7]. A methanol solution saturated with zinc acetate dihydrate (2.0 mL) was added to the chloroform solution (50 mL) of the material and stirred at rt for 5 h. The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. This residue was purified by silica gel column chromatography eluting with benzene to give a zinc porphyrin mixture (66.6 mg). The methanol solution (2.0 mL) of 35% aqueous HCl (0.5 mL) was added to the chloroform solution (50 mL) of the zinc porphyrin, and stirred at rt for 5 h. The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluting with chloroform/acetone (9/1) to give pure free base porphyrin as purple solids (61.5 mg, 0.0692 mmol, 8.1%). ^{1}H NMR (600 MHz, $CDCl_3$) δ −2.91 (s, 2H, NH), 3.47 (s, 3H, imidazole-Me), 7.52 (d, J = 1.2 Hz, 1H, imidazole), 7.70 (d, 1H, J = 1.2 Hz, imidazole), 8.88 (br, 2H, pyrrole), 8.91 (br, 4H, pyrrole), 8.94 (br, 2H, pyrrole); ^{19}F NMR (564 MHz, $CDCl_3$) δ −162.43 (ddd, J = 24.3, 20.9, 7.3 Hz, 2F, phenyl-*m*), −162.27 (ddd, J = 24.3, 24.3, 10.2 Hz, 1F, phenyl-*m*), −162.07 (ddd, J = 24.3, 24.3, 10.2 Hz, 1F, phenyl-*m*), −161.93 (ddd, J = 24.3, 20.9, 7.3 Hz, 2F, phenyl-*m*), −152.20 (td, J = 20.9, 10.7 Hz, 2F, phenyl-*p*), −152.16 (td, J = 24.3, 7.3 Hz, 1F, phenyl-*p*), −137.60 (dd, J = 24.3, 10.7 Hz, 2F, phenyl-*o*), −137.51 (dd, J = 24.3, 7.3 Hz, 1F, phenyl-*o*), −137.04 (dd, J = 24.3, 10.7 Hz, 2F, phenyl-*o*), −137.03 (dd, J = 24.3, 7.3 Hz, 1F, phenyl-*o*); MALDI-TOF MS *m*/*z* 889.6 (M + H$^+$), Calcd for $C_{42}H_{15}F_{15}N_6$, 888.1; HRMS *m*/*z* 889.1198 (M + H$^+$), Calcd for $C_{42}H_{16}F_{15}N_6$, 889.1197; UV–vis ($CHCl_3$) λ_{max} (Abs. ratio) 415(1), 507(0.074), 585(0.024), 637(0.0029) nm; fluorescence (λ_{Ex} 415 nm, $CHCl_3$) λ_{Em} 641, 710 nm.

2.3.2. 5-(1-Methyl-2-imidazolyl)-10,15,20-triphenylporphyrin, $ImTPPH_2$

1-Methyl-2-imidazolecarboxaldehyde (5.0 g, 45.4 mmol, 1.0 eq.) and benzaldehyde (16.9 g, 159 mmol, 3.5 eq.) were dissolved in refluxing propionic acid (700 mL). A solution of