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Synthesis, Characterization, and Autoreduction of a Highly Electron-Deficient Porphycenatoiron(III) with Trifluoromethyl Substituents

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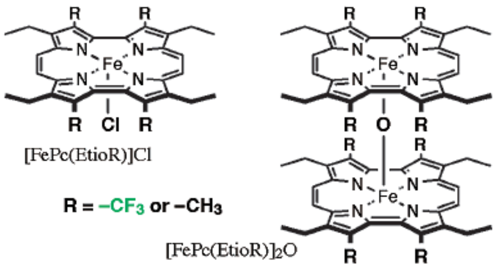
The synthesis of the first fluorine-containing iron porphycenes, 2,7,12,17-tetraethyl-3,6,13,16-tetrakis(trifluoromethyl)porphycenatoiron(III) chloride [FePc(EtioCF$_3$)]Cl and its μ-oxo dimer [FePc(EtioCF$_3$)]$_2$O and their characterizations are reported. The crystal structure of [FePc(EtioCF$_3$)]$_2$O displays a severe saddled distortion of the porphycene framework due to the steric and electronic effects of the CF$_3$ substituents. The oxidation and reduction potentials for the μ-oxo dimer are significantly more positive compared to those observed for the reference μ-oxo dimer of the iron porphycenes and porphyrins having no electron-withdrawing substituent. Moreover, the ^{1}H and ^{19}F NMR spectra of [FePc(EtioCF$_3$)]$_2$O demonstrated that the μ-oxo dimer is readily converted into the monomeric ferrous complex in pyridine-d_5 through autoreduction for 1 day, although the reduction of the reference iron porphycenes and porphyrins are not observed in pyridine. These results indicate that the trifluoromethylated iron porphycene is a highly electron-deficient complex with a pyrrolic macrocycle ligand.

Metalloporphycene,[1,2] a structural isomer of metalloporphyrin, has attracted considerable interest not only as a powerful probe to understand the physicochemical properties of a series of pyrrolic macrocycles[3] but also as a useful reactant such as a catalyst.[4,5] One of the important characteristics of the porphycene system is that the LUMO energy level of the ring is clearly stabilized due to the decrease in the symmetry of the macrocycle.[6,7] Therefore, it is expected that a porphycene with strong electron-withdrawing substituents will show a unique nature compared with porphyrins. However, the variety of peripheral groups substituted on the porphycene framework is limited and almost all known porphycenes have only peripheral alkyl substituents on the framework.[3] To further explore the striking features of metalloporphycenes, we are investigating the synthesis of a new type of porphycene and its metal complex.[8] Here, we wish to report the first synthesis of the trifluoromethylated iron porphycenes, 2,7,12,17-tetraethyl-3,6,13,16-tetrakis(trifluoromethyl)porphycenatoiron(III) chloride [FePc(EtioCF$_3$)]Cl, and its μ-oxo dimer [FePc(EtioCF$_3$)]$_2$O, their characterizations, and unusual reactivity due to the substitution of the strong electron-withdrawing CF$_3$ groups at the porphycene framework.

Chart 1. β-Substituted Iron Porphycene



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(8) 2,7,12,17-Tetraethyl-3,6,13,16-tetrakis(trifluoromethyl)porphycene, H$_2$Pc(EtioCF$_3$), has been recently prepared. The first reduction potential of H$_2$Pc(EtioCF$_3$) is approximately 1.2 V more positive compared to that for a series of usual porphyrins. Hayashi, T.; Nakashima, Y.; Ito, K.; Ikegami, T.; Suzuki, A.; Hisaeda, Y. *Org. Lett.* **2003**, *5*, 2845−2848.

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Monomeric [FePc(EtioCF$_3$)]Cl was not directly obtained from the reaction of the free base H$_2$Pc(EtioCF$_3$)[8] with FeCl$_3$ or Fe(acac)Cl,[7,9,10] since the monomeric iron complex was easily converted into the μ-oxo dimer, [FePc(EtioCF$_3$)]$_2$O, during the purification in spite of no treatment under alkali conditions. The cleavage of the dimer into the monomer requires stirring the dimer solution in the presence of TFA/0.1 N HCl for over 30 min.

[FePc(EtioCF$_3$)]Cl and [FePc(EtioCF$_3$)]$_2$O were characterized by UV−vis, ^{1}H and ^{19}F NMR, and MS spectroscopies. The optical spectra of these iron complexes exhibit a significant red shift with respect to 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycenatoiron(III) chloride, [FePc(EtioCH$_3$)]Cl, and its μ-oxo dimer, [FePc(EtioCH$_3$)]$_2$O in CHCl$_3$. For example, the characteristic Q-band of [FePc(EtioCF$_3$)]$_2$O is 54 nm red-shifted from that of [FePc(EtioCH$_3$)]$_2$O. These significant red shifts of their absorption maxima are similar to a series of perhalogenoporphyrinatoirons due to the electron-withdrawing effect.[11] The ^{19}F NMR spectrum of [FePc(EtioCF$_3$)]Cl in CDCl$_3$ shows a broad peak at 67.42 ppm due to the high-spin iron center, and the resonance is shifted by more than 50 ppm downfield from that of the corresponding iron porphyrin.[12,13] In the case of [FePc(EtioCF$_3$)]$_2$O, the ^{19}F resonance shifted upfield at −45.36 ppm due to antiferromagnetic coupling.

Figure 1 shows the molecular structure of [FePc(EtioCF$_3$)]$_2$O recrystallized from CHCl$_3$ and 2-propanol. The complex exists in the crystal as a molecule with C_2 symmetry, and two iron porphycenes show the highly distorted square-pyramidal coordination with the saddle-shape configuration. The μ-oxo dimer was found to possess a completely linear Fe−O−Fe angle due to the steric bulky CF$_3$ substituents between the two porphycene rings. The two Fe−O bond lengths in [FePc(EtioCF$_3$)]$_2$O are 1.753(4) and 1.755(4) Å, and the two iron atoms are displaced by 0.630 and 0.541 Å from the least-squares plane in [FePc(EtioCF$_3$)]$_2$O through the four porphyrin nitrogen atoms. These values are almost comparable with those observed in the reported μ-oxo dimers of the iron porphycenes and porphyrins.[14] In contrast, the displacements of the pyrrole β-carbon atoms from the N4 mean planes vary from −0.836 to 0.339 Å, which are significantly larger values than those observed in the reference compound of [FePc(EtioCH$_3$)]Cl (−0.451 to 0.092 Å).[15] The average of the four pyrrole−pyrrole dihedral angles in [FePc(EtioCF$_3$)]$_2$O is 23.13°, which is significantly larger than that observed in a series of the μ-oxo dimers[14] or [FePc(EtioCH$_3$)]Cl with a 4.80° dihedral angle.[15] These findings indicate that the substitution of the four electron-withdrawing CF$_3$ groups produces the severe saddle-shaped deformation of the aromatic framework.

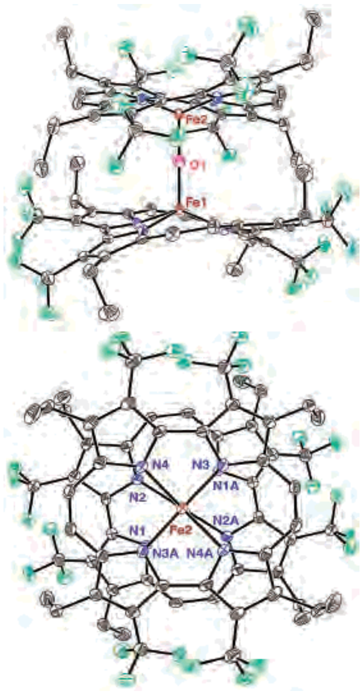

Figure 1. ORTEP diagram of [FePc(EtioCF$_3$)]$_2$O with thermal ellipsoids drawn at 50% probability. Top: side view. Bottom: top view. For clarity, solvent and hydrogen atoms are omitted (color scheme: Fe, orange; O, red; C, gray; N, blue; F, green).

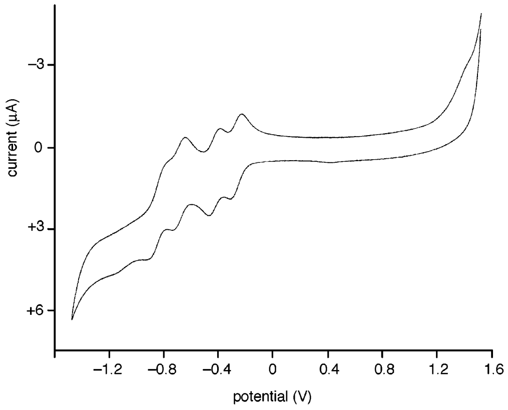

Figure 2. Cyclic voltammogram of [FePc(EtioCF$_3$)]$_2$O in CH$_2$Cl$_2$, 0.1 M TBAP. Scan rate = 0.1 V/s. Reference electrode: Ag/AgCl.

Electrochemistry of [FePc(EtioCF$_3$)]$_2$O clearly reveals the significant effect on the substitution of the electron-withdrawing groups on the porphycene framework as shown in Figure 2. First, the oxidation process of [FePc(EtioCF$_3$)]$_2$O was not observed by conventional analysis in CH$_2$Cl$_2$, since the oxidation could occur outside the solvent/electrolyte

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(15) We have never determined the molecular structure of [FePc(EtioCF$_3$)]Cl, whereas the single crystal of [FePc(EtioCH$_3$)]Cl was obtained. According to the 3D structure of [FePc(EtioCH$_3$)]Cl, the chloride coordinates to the iron atom with an Fe−Cl distance of 2.2340(6) Å. Hayashi, T.; Aritome, I.; Nakashima, Y.; Hisaeeda, Y. Unpublished results.

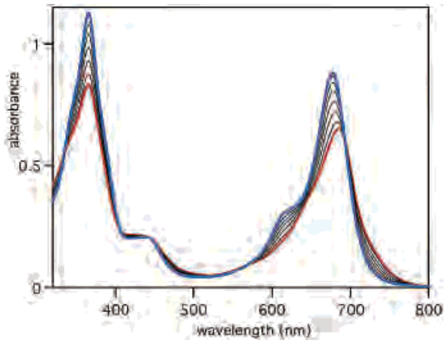

Figure 3. Spectral changes of $[FePc(CF_3)_4]_2O$ in pyridine at 25 °C. Red and blue spectra are obtained after 0 and 40 h, respectively.

potential window. This result suggests that the first oxidation potential could be higher than +1.3 V (vs Ag/AgCl), although $[FePc(EtioCH_3)]_2O$ undergoes four one-electron oxidations in the range 0.69−1.22 V. Second, the four reductions of $[FePc(EtioCF_3)]_2O$ occurred at $E_{1/2} = -0.29$, −0.45, −0.71, and −0.86 V, which are approximately 800 mV more positive than those observed in $[FePc(EtioCH_3)]_2O$.[7,16] These results emphasize the fact that the drastic shifts in the oxidation and reduction potentials are derived from the combination of the characteristics of the porphycene framework and the substitution of the strong electron-withdrawing CF_3 groups at the pyrrolic β-carbons.

To evaluate the Lewis acidity and redox property of the porphycene iron atom, we monitored the reaction of the complexes with pyridine. The UV−vis spectrum of $[FePc(EtioCF_3)]_2O$ in pyridine under anaerobic conditions produced significant changes over 40 h via clear isosbestic points as shown in Figure 3. The final spectrum is consistent with that observed for the Fe(II)−pyridine complex, $[FePc(EtioCF_3)](py)_2$,[6,17,18] which was prepared by the reduction of $[FePc(EtioCF_3)]Cl$ with dithionite and the following addition of pyridine. These interesting findings are supported by ^1H and ^{19}F NMR experiments; the ^1H NMR spectrum of a pyridine-d_5 solution with $[FePc(EtioCF_3)]_2O$ after 1 day showed the diamagnetic signals, and a sharp ^{19}F peak appeared at −53.06 ppm. The observed proton and fluorine chemical shifts are comparable with those observed for the free base porphycene, $H_2Pc(EtioCF_3)_4$, suggesting that the new species is the monomeric low-spin Fe(II) porphycene coordinated with pyridine molecules. In contrast, the reference μ-oxo dimer $[FePc(EtioCH_3)]_2O$ in pyridine-d_5 was also converted into the monomer, but the resulting species was a low-spin Fe(III) bispyridine complex, $[FePc(EtioCH_3)](X)(py)_2$, determined by a ^1H NMR experiment.[19] This sharp difference indicates that the only $[FePc(EtioCF_3)]_2O$ can be easily reduced through the cleavage of the dimer in pyridine. Moreover, to the best of our knowledge, there has been no case in which the pyridine induces the autoreduction of the Fe(III) porphyrin or its derivatives except for dioxoporphodimethene ferric complex.[20−22] The observed monomerization and the following autoreduction of $[FePc(EtioCF_3)]_2O$ upon dissolution in pyridine are very indicative of the facts that the iron atom ligated by the porphycene framework has strong Lewis acidity and the four trifluoromethyl substituents shift the redox potential of the iron to significantly positive.

In conclusion, we have demonstrated the first example of fluorine-containing iron porphycene which demonstrates unusual structure, redox potentials, and reactions such as autoreduction of ferric species. Thus, the introduction of strong electron-withdrawing groups at the β-pyrrolic carbons of the porphycene framework will serve as a new way to create a highly electron-deficient macrocycle and/or metal center with unique reactivity.

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Supporting Information Available: Experimental details, NMR spectra, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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