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Synthesis, Structure, and Chemical Property of the First Fluorine-Containing Porphycene

Takashi Hayashi,[*,†,‡] Yuji Nakashima,[†] Kazuyuki Ito,[†] Takahiro Ikegami,[†]
Isao Aritome,[†] Akihiro Suzuki,[§] and Yoshio Hisaeda[*,†]

Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University, Fukuoka 812-8581, and Department of Material Engineering,
Nagaoka National College of Technology, Nagaoka 940-8532, Japan

thayatcm@mbox.nc.kyushu-u.ac.jp

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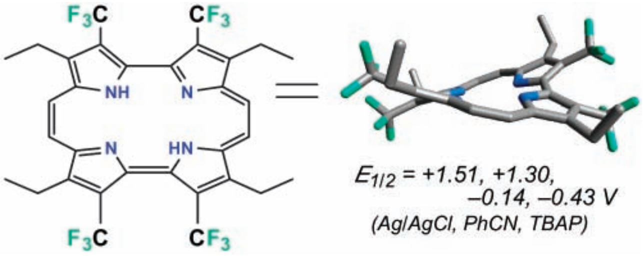
ABSTRACT



A pyrrolic macrocycle, β-tetrakis(trifluoromethyl)porphycene, is the first example of a fluorine-containing porphycene. Four electron-withdrawing CF_3 substituents provide a highly distorted structure and an attractive electron-deficient nature for the porphycene framework. From the electrochemical study, it is found that the LUMO energy level for the β-trifluoromethylporphycene is 1.24 V more stabilized compared to that for etioporphyrin. Moreover, the deprotonation of the inner N–H proton in the porphycene was observed upon the addition of DBU.

Over the last two decades, a variety of free bases and metal complexes of fluorinated porphyrins, perfluoroalkyl or perfluoroaryl porphyrins have been prepared, because the electron-deficient porphyrins have been very useful not only for understanding the physicochemical properties of tetrapyrrolic macrocycles but also for utilization as oxidation catalysts.[1] One of the interesting aspects of the fluorine-containing porphyrins is that the oxidation and reduction potentials are relatively more positive than those of the corresponding usual porphyrins.[2] Furthermore, it has often been found that the structure of the electron-deficient porphyrins is highly distorted due to the steric and/or electronic effects of electron-withdrawing substituents.[3] Therefore, considerable effort has been devoted to studying unique porphyrins with strongly electron-withdrawing groups. In contrast, it is known that a porphycene, a structural isomer of porphyrin,[4,5] reveals that the reduction potentials are also clearly shifted to a more positive value despite having no electron-withdrawing substituents bound at the porphycene framework,[6,7] because of the lower symmetry of the por-

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[†] Kyushu University.
[‡] Member of Japan Science and Technology Corporation (JST).
[§] Nagaoka National College of Technology.

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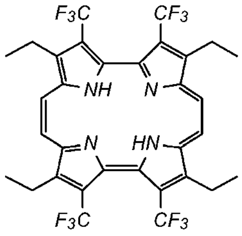
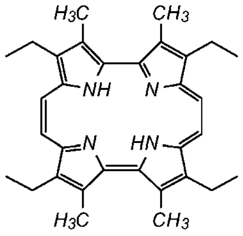
phycene compared to the geometry of the corresponding porphyrin.[8] Therefore, a modified porphycene incorporating a CF_3 or perfluoroalkyl group at the peripheral β-pyrrolic position will attract considerable interest as a highly electron-deficient tetrapyrrolic macrocycle, although, to the best of our knowledge, there is no report describing the preparation of a fluorine-containing porphycene.[9] Recently, we have synthesized the first trifluoromethylated porphycene, 2,7,-12,17-tetraethyl-3,6,13,16-tetrakis(trifluoromethyl)porphycene, H_2Pc(EtioCF$_3$), which seems to be an analogue of etioporphycene, 2,7,12,17-tetraethyl-3,6,13,16-tetramethylporphycene, H_2Pc(EtioCH$_3$).[10] As detailed below, the structure, electrochemical property and unique reactivity of H_2Pc(EtioCF$_3$) suggest that the β-trifluoromethylated porphycene falls into the category of the highest electron-deficient tetrapyrrolic macrocycles.

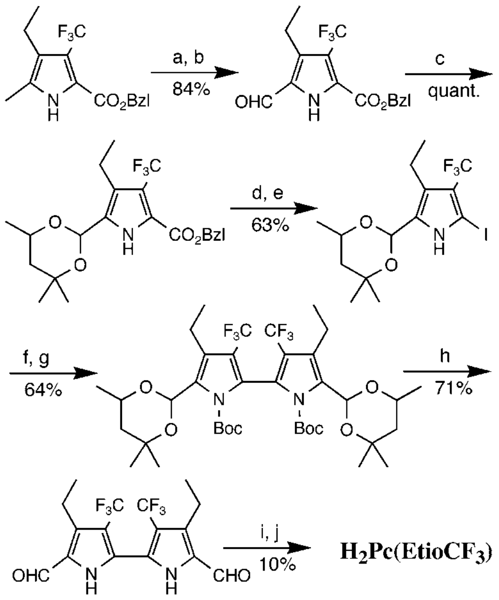


H_2Pc(EtioCF$_3$)



H_2Pc(EtioCH$_3$)

Scheme 1[a]



[a] Reaction conditions: (a) Br_2, SO_2Cl_2, AcOH, TFA, Ac_2O; (b) H_2O; (c) hexylene glycol, *p*-TsOH, benzene; (d) Pd/C, H_2, Et_3N, THF; (e) KI, I_2, H_2O; (f) Boc_2O, DMAP, CH_2Cl_2; (g) Cu, DMF; (h) concentrated HCl, AcOH; (i) $TiCl_4$, Zn, CuCl, THF; (j) DDQ, $CHCl_3$.

As shown in Scheme 1, the synthesis of H_2Pc(EtioCF$_3$) started from the preparation of trifluoromethylpyrrole.[11] Although an α-methyl group of the pyrrole ring is generally oxidized to a carboxyl group through halogenation of the methyl group by treatment with Br_2 and SO_2Cl_2,[12] we obtained α-formylpyrrole under similar conditions in quantitative yield, because the CF_3 group might reduce the reactivity of halogenation at the α-methyl group. After the formyl group was protected by hexylene glycol, deprotection of the benzyl ester and decarboxylative iodination led to an activated α-iodopyrrole. An α,α′-diformylbipyrrole, a precursor of H_2Pc(EtioCF$_3$), was achieved by Ullmann coupling of the α-iodopyrrole and the following deprotection of acetal in 45% yield. The cyclization of two 5,5′-diformyl-2,2′-bipyrrole molecules in the presence of $TiCl_4$ via the reductive McMurry coupling gave a light-yellow oil as an initial condensation product that could be a dihydroporphycene species, although it has never been purified and characterized. After the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DDQ, into the solution of the intermediate species, a greenish blue 18π-electron aromatic porphycene, H_2Pc(EtioCF$_3$), was obtained in 10% yield. In the case of normal porphycene synthesis, the aromatization due to the autoxidation occurs spontaneously under ambient atmosphere after the McMurry cyclization. This finding suggests that an oxidant such as DDQ is required to prepare H_2Pc(EtioCF$_3$), because the coupling intermediate is not readily oxidized.[13]

The porphycene H_2Pc(EtioCF$_3$) was characterized by UV−vis, ^{1}H and ^{19}F NMR, and mass spectroscopy. The λ_{max} values of the Q-band in the UV−vis spectrum for H_2Pc(EtioCF$_3$) appeared at 622, 670, and 719 nm in CH_2Cl_2, which showed a 52−63 nm red shift with respect to those observed for H_2Pc(EtioCH$_3$) as shown in Figure 1. The significant Q-band shift, which is often seen in a series of porphyrins with bulky electron-withdrawing groups,[14−18] indicates that the HOMO−

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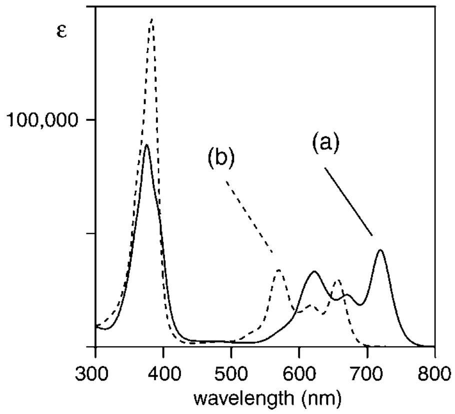

Figure 1. Electronic absorption spectra of (a) $H_2Pc(EtioCF_3)$ and (b) $H_2Pc(EtioCH_3)$ in CH_2Cl_2.

LUMO energy gap decreases with respect to that for $H_2Pc(EtioCH_3)$. The ^1H NMR spectrum of $H_2Pc(EtioCF_3)$ in $CDCl_3$ is comparable with that observed for $H_2Pc(EtioCH_3)$ except for the internal NH proton resonance.[10] The NH proton of $H_2Pc(EtioCF_3)$ was found to resonate at 2.33 ppm, which is 1.47 ppm lower than that for $H_2Pc(EtioCH_3)$. This result probably comes from the increase in the hydrogen-bonding interaction of NH proton with the pyrrole imine nitrogen and/or the decrease in the aromatic ring current due to the distorted structure.

The molecular structure of $H_2Pc(EtioCF_3)$ determined by X-ray crystallographic analysis is shown in Figure 2. The framework of $H_2Pc(EtioCF_3)$ is found to show a saddle-distorted structure that is not seen for the planar structure of normal porphycene such as $H_2Pc(EtioCH_3)$.[10a] Particularly, each bipyrrole is strongly twisted along the pyrrolic Cα−Cα′ axis to reduce the steric and electronic repulsion of the two adjacent CF_3 groups; the average values of the pyrrole−pyrrole dihedral angles for $H_2Pc(EtioCF_3)$ and $H_2Pc(EtioCH_3)$ are 29.50 and 10.50°, respectively. Therefore, the displacement of the pyrrolic β-carbon from the average plane defined by the four pyrrole nitrogen atoms is determined to be a maximum of 0.976 Å for $H_2Pc(EtioCF_3)$, whereas the same value for $H_2Pc(EtioCH_3)$ is 0.307 Å.[10a] These comparisons demonstrate that $H_2Pc(EtioCF_3)$ reveals the most distorted structure among the known porphycene compounds.[8]

The redox potentials of $H_2Pc(EtioCF_3)$ and $H_2Pc(EtioCH_3)$ were measured by cyclic voltammetry in PhCN. First and second reduction peaks were observed with each reversible one-electron-transfer separation ($E_{pa} - E_{pc} = 92$ and 100 mV, respectively, for $H_2Pc(EtioCF_3)$) in PhCN, whereas we determined the first and second oxidation potentials by differential pulse voltammetry, because clear reversible peaks were not detected under the normal condition.[7,19] Table 1 summarizes the comparative oxidation and reduction potentials for the porphycenes and the corresponding porphyrins.

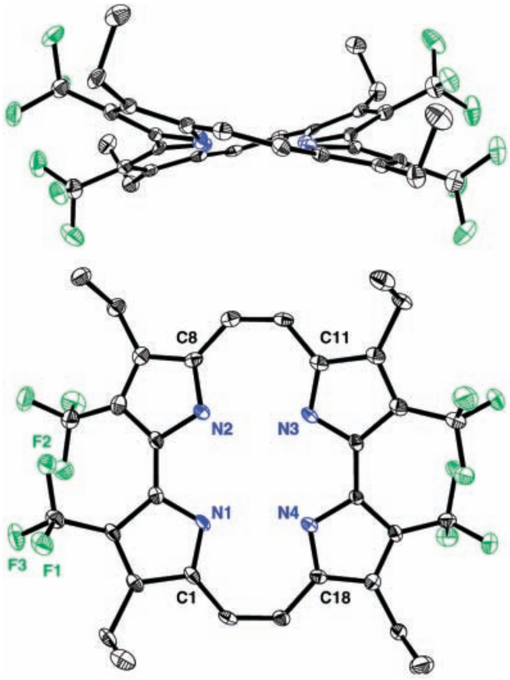

Figure 2. ORTEP drawings of $H_2Pc(EtioCF_3)$ with thermal ellipsoids at 50% probability. Top: perspective view. Bottom: macrocycle plane view. For clarity, only N atoms and selected C and F atoms have been numbered and hydrogen atoms have been omitted.

In a manner similar to a series of free-base porphycenes, the first reduction of $H_2Pc(EtioCH_3)$ occurs at a 0.46 V less negative potential than that for 2,7,12,17-tetramethyl-3,8,13,18-tetraethylporphyrin, $H_2Por(EtioCH_3)$, due to splitting of the π* molecular orbitals with a decrease in the symmetry of the tetrapyrrolic macromolecule, whereas the first oxidation potential of $H_2Pc(EtioCH_3)$ is comparable with that observed for $H_2Por(EtioCH_3)$.[6,7] Interestingly, $H_2Pc(EtioCF_3)$ is reduced at a potential of −0.14 V (vs Ag/AgCl) in PhCN;

Table 1. Comparative Oxidation and Reduction Potentials (V, Ag/AgCl) for Free-Base Porphycenes and Porphyrins[a]

	oxidation	reduction	solvent	source of data
$H_2Pc(EtioCF_3)$	$+1.30^b$ $+1.51^b$	−0.14 −0.43	PhCN	this work
$H_2Pc(EtioCH_3)$	$+0.92^b$ $+1.26^b$	−0.92 −1.21	PhCN	this work
$H_2Por(EtioCH_3)$	$+0.93^b$ $+1.38^b$	−1.38	PhCN	this work
$H_2Por(EtioCF_3)^{c,d}$	+0.84 +1.22		CH_2Cl_2	ref 20

[a] Potential values were measured using cyclic voltammetry (100 mV/sec). The ferrocene/ferrocenium redox couple (0.51 V vs Ag/AgCl) was used as the internal standard. [Porphycene] = 1.4×10^{-3} M; [TBAP] = 0.1 M. [b] These oxidation potentials were determined by a differential pulse voltammetry technique. [c] $H_2Por(EtioCF_3)$ = 2,7,12,17-tetramethyl-3,8,13,18-tetrakis(trifluoromethyl)porphyrin. [d] These potentials were measured in the presence of TBAP, and the reference electrode was $Ag/AgClO_4$ (ref 20).

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[19] In the cyclic voltammetry experiment, E_{pa} peaks were clearly observed at 1.36 and 1.62 V for $H_2Pc(EtioCF_3)$.

this first reduction potential is 0.78 V more positive than that observed for $H_2Pc(EtioCH_3)$, indicating that a remarkable stabilization of the LUMO energy level results from the introduction of four strongly electron-withdrawing CF_3 substituents at the β-pyrrole positions. In fact, a significant positive shift upon the introduction of electron-withdrawing groups has also been seen in porphyrin chemistry (e.g., the value of the first reduction potential for β-tetrakis(trifluoromethyl)tetraphenylporphyrin is ca. 0.8 V more positive compared to that of tetraphenylporphyrin).[18b] The first oxidation of $H_2Pc(EtioCF_3)$ occurs at a potential of $+1.30$ V, which is 0.38 V higher than that observed for $H_2Pc(EtioCH_3)$. Therefore, the stabilization of the one-electron oxidation and reduction states does not occur to the same degree; the positive shift in the oxidation state for $H_2Pc(EtioCF_3)$ is less than half that observed in the reduction potential. These results suggest that the HOMO energy level is destabilized due to the distortion of the porphycene structure of $H_2Pc(EtioCF_3)$, as shown in Figure 2.[21−23]

In addition, it is of interest to discuss the HOMO−LUMO energy gap electrochemically determined from the difference between the first reduction and oxidation potentials described above. The gap for $H_2Pc(EtioCH_3)$ ($\Delta E = E_{ox1} - E_{red1} = 1.84$ V) is clearly smaller than that observed in normal porphyrins ($\Delta E = 2.31$ V for $H_2Por(EtioCH_3)$).[7] Furthermore, the dramatic HOMO−LUMO gap decrease to 1.44 V for $H_2Pc(EtioCF_3)$ was observed due to the introduction of strongly electron-withdrawing groups on the porphycene framework. The significantly smaller HOMO−LUMO gap for $H_2Pc(EtioCF_3)$ is clearly indicative of the large red-shifted Q-band in the optical spectrum. As seen in several electron-deficient porphyrins, it is concluded that the reduced gap value comes from the electronic effect of the strongly electron-withdrawing CF_3 groups and the distorted macrocycle structure.[14,15,17,18,21a]

The electron-deficient property of the tetrapyrrolic ligand was also evaluated by monitoring the deprotonation of the inner N−H proton to yield a monoanion species upon the addition of a base such as 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).[16,18b] The addition of an excess of DBU to a CH_2Cl_2 solution containing $H_2Pc(EtioCH_3)$ ($[DBU]/[H_2Pc(EtioCH_3)] > 10^4$) caused no spectral changes in the Soret and Q-band regions under our conditions, indicating that the inner protons of $H_2Pc(EtioCH_3)$ were much less acidic than the protonated DBU ($DBUH^+$). In contrast, drastic changes in the optical spectrum of $H_2Pc(EtioCF_3)$ were observed upon the addition of DBU, and the color of the solution turned purple. The difference in pK_a values between $H_2Pc(EtioCF_3)$ and $DBUH^+$ was 1.2 ± 0.5 in CH_2Cl_2.[24] Furthermore, the addition of triethylamine to CH_2Cl_2 solution containing $H_2Pc(EtioCF_3)$ also led to the same spectral changes. These titrimetric measurements with DBU or triethylamine support the facts that the inner N−H of $H_2Pc(EtioCF_3)$ is more acidic than that of $H_2Pc(EtioCH_3)$ or $H_2Por(EtioCH_3)$, indicating that the monoanion species of $H_2Pc(EtioCF_3)$, $HPc(EtioCF_3)^-$, is stabilized by the inductive effect of the σ-electron-withdrawing CF_3 substituents.

In conclusion, we have synthesized the first fluorine-containing porphycene, which exhibits an extremely electron-deficient nature. Particularly, the substitution of CF_3 groups at the β-pyrrolic carbon effectively stabilizes the LUMO energy level by 1.24 V compared to general porphyrins such as $H_2Por(EtioCH_3)$. The present results indicate that *the combination of the porphycene framework and the strongly electron-withdrawing substituents* gives us a new family of highly electron-deficient tetrapyrrolic macrocycles that will be very attractive for creating a new metal complex as a catalyst.

Acknowledgment. This work was partially supported by the Kurata Memorial Hitachi Science and Technology Foundation.

Supporting Information Available: Experimental procedures and compound characterization data and X-ray crystallographic data for $H_2Pc(EtioCF_3)$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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