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[24]Pentaphyrin(2.1.1.1.1): a Strongly Antiaromatic Pentaphyrin

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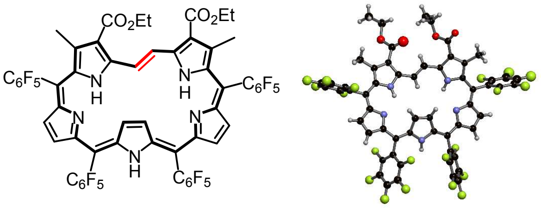
Supporting Information Placeholder

ABSTRACT: [24]Pentaphyrin(2.1.1.1.1) **1** was synthesized by dehydrogenation of dihydropentaphyrin(2.1.1.1.1) **2** as the first example of vinylogous pentaphyrin. Pentaphyrin **1** takes a roughly planar structure and shows strong antiaromatic character, reflecting 24π-conjugated circuit. In spite of the antiaromatic character and the relatively small circuit, **1** is stable under ambient conditions.



[24]Pentaphyrin(2.1.1.1.1)
Stable and Storongly Antiaromatic Vinylogous Expanded Porphyrin

Expanded porphyrins are conjugated macrocycles with more than four pyrrole units, which have been demonstrated to realize various electronic states including Hückel aromatic and antiaromatic, Möbius aromatic and antiaromatic, and radical species.[1] Among these, pentaphyrins and their core-modified variants[2] constitute a unique class of conjugated macrocycles in light of the optical properties suitable for photodynamic therapy and light-harvesting, and the intrinsic strain to take planar structures.[3] As the representative example, sapphyrins ([22]pentaphyrin(1.1.1.1.0)s) were first reported by Woodward et al and extensively developed by Sessler et al.[4] Sapphyrins are planar 22π aromatic molecules consisting of two imino-type pyrroles and three amino-type pyrroles. Pentakis(pentafluorophenyl)-substituted pentaphyrin was formed as a N-fused molecule presumably as a consequence of its large steric strain.[5] Recently, we reported the synthesis of meso-unsubstituted [22]pentaphyrin(1.1.1.1.1), which existed as a planar non-fused pentaphyrin with two intramolecular hydrogen bonds.[6] This pentaphyrin is spared the steric strain and thus strongly aromatic. (Chart 1)

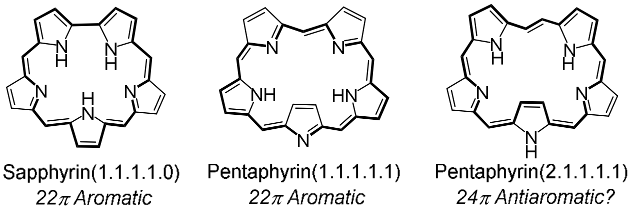


Chart 1. Skeletons of pentaphyrins. Their π-conjugation circuits are shown in bold lines.

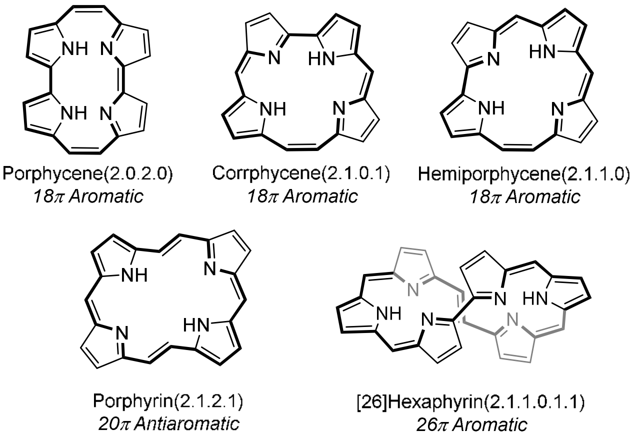
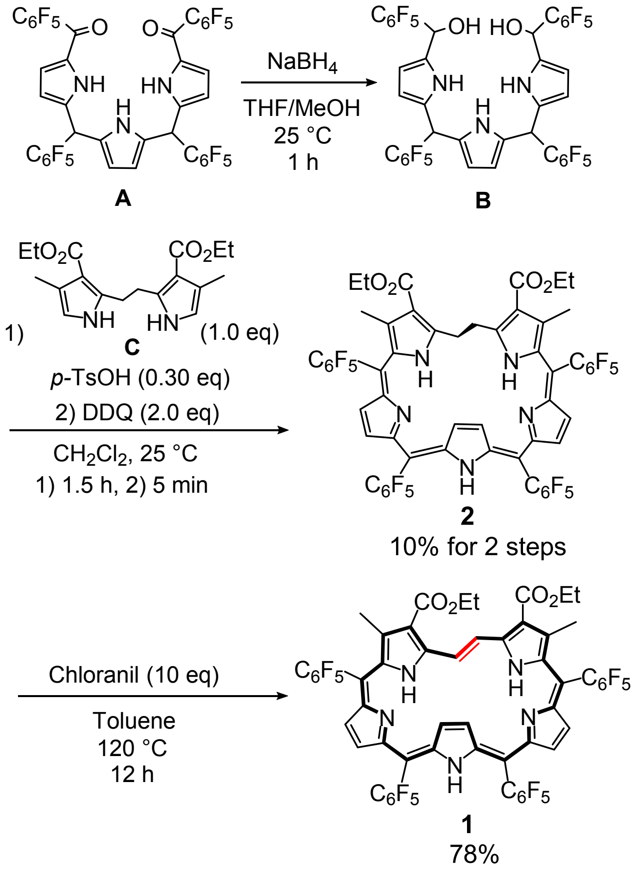


Chart 2. Selected examples of porphyrinoids with vinylene bridges at meso-positions.

In the course of this work, we become interested in [24]pentaphyrin(2.1.1.1.1) that possesses a vinylene bridge along the conjugation circuit (Chart 1). While various tetrapyrrolic macrocycles having vinylene bridges such as porphycene (porphyrin(2.0.2.0)),[7] corrphycene(2.1.0.1),[8] homoporphyrin(2.1.1.1),[9] hemiporphyrcene(2.1.1.0),[10] and [20]porphyrin(2.1.2.1),[11] were reported, there are only a limited number of expanded porphyrins possessing a vinylene bridge along the conjugation circuit. As an interesting example, [26]- and [28]hexaphyrin(2.1.1.0.1.1) were formed via transposition of the *meso*-carbon during boron(III) insertion into [28]hexaphyrin(1.1.1.1.1.1) (Chart 2).[12] Some core-modified vinylene-bridged expanded porphyrins were also reported.[13] In this paper, we report the synthesis of [24]pentaphyrin(2.1.1.1.1) **1** as the first example of vinylogous pentaphyrin. Curiously, pentaphyrin **1** is rather stable under ambient conditions despite its distinct antiaromatic character and relatively small size of the conjugation circuit.



Scheme 1. Synthesis of dihydropentaphyrin 2 and [24]pentaphyrin(2.1.1.1.1) 1.

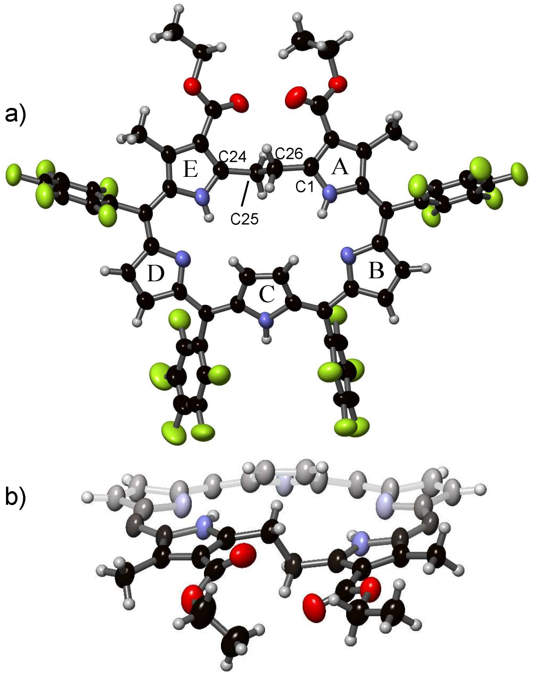


Figure 1. X-Ray crystal structure of dihydropentaphyrin **2** obtained from acetonitrile/water solution. a)Top view and b)side view. Solvent molecules and *meso*-pentafluorophenyl groups in side view are omitted. Thermal ellipsoids are shown in 50% probability.

Following our previous work,[6b] we employed a hybrid synthetic protocol by using meso-aryl tripyrrane and β-substituted dipyrrole. After reduction of 1,14-pentafluorobenzoyl-5,10-pentafluorophenyl tripyrrane **A**, the obtained tripyrrane dicarbinol **B**[14] and 1,2-bis(3-ethoxycarbonyl-4-methylpyrrol-2-yl)ethane **C**[8b,15] in CH_2Cl_2 were treated with 0.3 equivalent of *p*-toluenesulfonic acid under nitrogen atmosphere, and the resulting mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). On a silica gel column, dihydropentaphyrin(2.1.1.1.1) **2** eluted as a brown band was separated (Scheme 1). Recrystallization with hexane gave pure **2** in 10% yield. High-resolution electrospray ionization time-of-flight mass spectroscopy (HR-ESI-TOF MS) indicated the parent ion peak of **2** at *m/z* =1240.1948 (calcd for $C_{58}H_{30}N_5F_{20}O_4^+$ $[M+H]^+$ = 1240.1973). The ^1H NMR spectrum of **2** showed two doublets at 6.82 and 6.55 ppm, and one singlet at 6.73 ppm due to the β-protons, two singlets at 11.96 and 7.12 ppm due to the NH protons, a quartet and a triplet at 4.39 and 1.36 ppm due to the ethoxy groups, and a singlet due to methyl groups at 2.11 ppm. These chemical shifts indicated nonaromatic character of its macrocycle. Additionally, a signal due to the four protons of the ethylene bridge was observed as a singlet at 2.87 ppm (Figure 3a). The structure of **2** has been confirmed by X-ray diffraction analysis to be a pentapyrrolic macrocycle, in which an ethylene(-CH_2CH_2-) unit bridges the pyrroles A and E (Figure 1).[16] The pyrrolic NH protons of the pyrroles A and E are hydrogen-bonded with the pyrrolic nitrogen atoms of the pyrroles B and D, respectively, while the pyrrole C is pointing outward, similar structurally to the mono-*meso*-unsubstituted [22]pentaphyrin(1.1.1.1.1).[6]

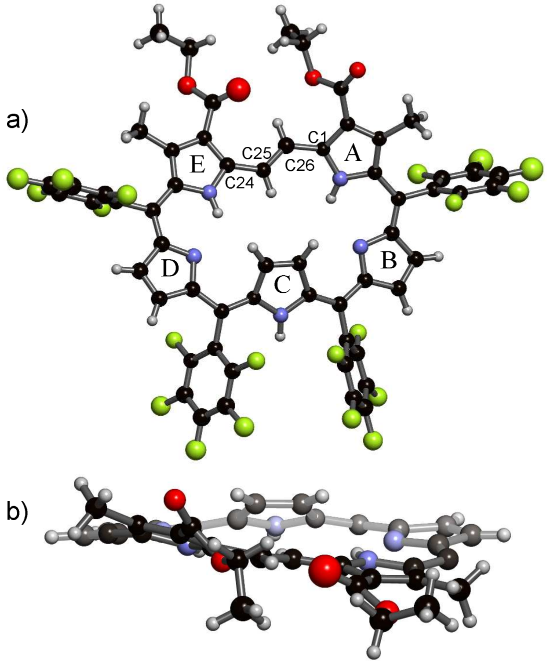


Figure 2. X-Ray crystal structure of pentaphyrin **1** obtained from chlorobenzene/nonane solution. a) Top view and b) side view.

Solvent molecules and *meso*-pentafluorophenyl groups in side view are omitted. Thermal ellipsoids are shown in 30% probability. One of two similar molecules in the symmetrical unit is shown.

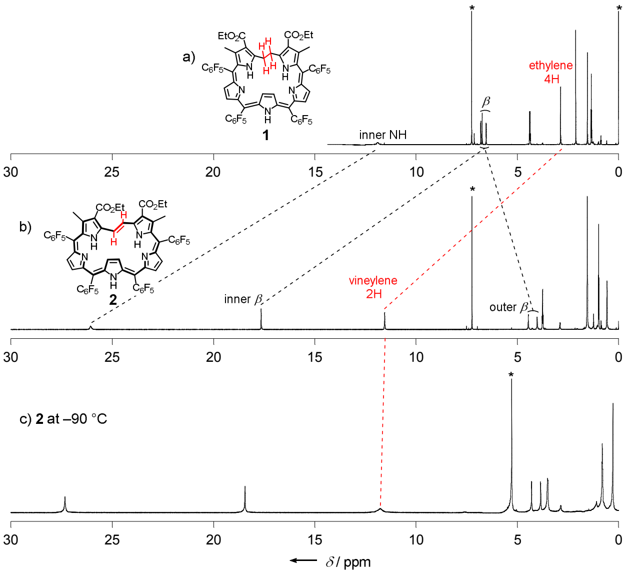


Figure 3. ^{1}H NMR spectra of a) **2** in $CDCl_3$ at room temperature and **1** b) in $CDCl_3$ at room temperature and c) in CD_2Cl_2 at –90 °C. * indicates residual solvent peaks.

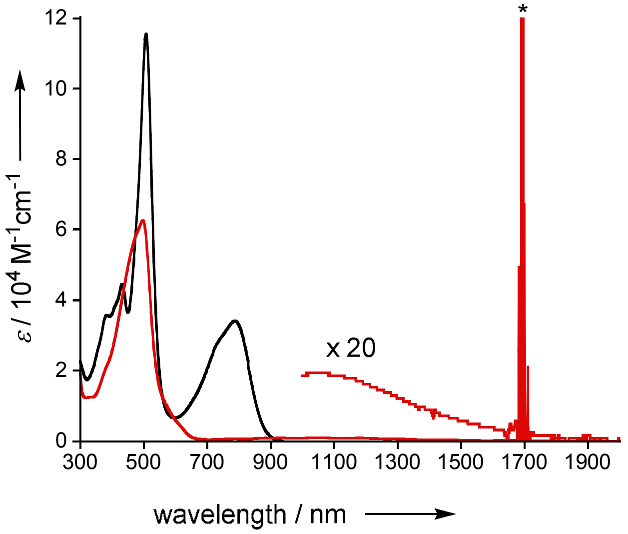


Figure 4. UV/Vis absorption spectra of **2**(black) and **1**(red) in CH_2Cl_2. *Vibration bands of solvent.

In the next step, we examined the dehydrogenation of **2**. Attempted dehydrogenation of **2** with excess DDQ led to its serious decomposition. After numerous experiments, we found that ethylene-selective dehydrogenation proceeded efficiently with 10 equiv. of *p*-chloranil in toluene at 120 ℃ to give [24]pentaphyrin(2.1.1.1.1) **1** in 78% yield (Scheme 1). To our delight, pentaphyrin **1** was very stable in the solid state and in solution indefinitely even in the aerobic conditions. HR-ESI-TOF MS indicated the parent ion peak of **1** at *m/z* =1236.1697 (calcd for $C_{58}H_{26}N_5F_{20}O_4^-$ [M-H]$^-$ = 1236.1671). Crystals of **1** suitable for X-ray diffraction analysis were obtained by diffusion of *n*-nonane into its chlorobenzene solution with one drop of water. In the unit cell, two different structures were found. Thus, we used averaged values in the following discussion. The structure of **1** has been revealed to be a roughly planar pentaphyrin(2.1.1.1.1). The formed C25-C26 double bond showed *E*-stereochemistry with a bond length of 1.34 Å. The largest dihedral angle was 18.9(17)° and the mean plane deviation (MPD) of the main pentaphyrin skeleton of **1** was calculated to be 0.269 Å (Figure 2).[17] Similar to **2**, the hydrogen bonding interaction between the pyrrolic NH protons of the pyrroles A and E with the nitrogen atoms of the pyrroles B and D is important to keep the planar structure. The strong antiaromaticity of its 24π conjugation circuit of **1** is indicated by its ^{1}H NMR spectrum that displays signals at 4.48 and 4.04 ppm due to the outer β protons, a singlet at 17.68 ppm due to the inner β protons, two singlets at 26.11 and 2.86 ppm due to outer and inner NH protons, and a quartet and a triplet at 3.77 and 1.00 ppm due to the ethoxy groups (Figure 3b). The ^{1}H signal of the *trans*-vinylene bridge was observed as a singlet at 11.57 ppm, indicating free rotation of the vinylene bridge at room temperature. At –90 °C in CD_2Cl_2, the signal of **1** was significantly broadened, suggesting that the rotation was considerably slowed down but not frozen (Figure 3c). The rotation of vinylene group is indicated to be faster than that of porphyrin(2.1.2.1).[11]

The UV/vis absorption spectrum of **2** exhibits a relatively sharp absorption band at 508 nm and a weak absorption band at 787 nm. These absorption bands are derived from the noncyclic conjugated pentapyrrolic unit. The absorption spectrum of **1** is totally different from that of **2**, displaying a broad Soret band at 498 nm and a very weak absorption up to about 1700 nm (Figure 4). The weak absorption can be ascribed to the presence of low-energy dark states, which are characteristic of antiaromatic porphyrinoids.[18]

Cyclic voltammetry (CV) measurements for **2** revealed reversible oxidation waves at 0.18 and 0.51 V and an irreversible reduction wave at -1.08 V versus a ferrocene/ferrocenium ion couple. On the other hand, **1** indicated reversible oxidation waves at 0.08 and 0.38 V and reduction waves at –0.90 and –1.11 V (see SI). The electrochemical HOMO–LUMO gaps were 1.26 eV for **2** and 0.98 eV for **1**. The smaller HOMO–LUMO gap of **1** than that of **2** was consistent with its antiaromatic character.

To obtain further insight into the physical properties of **1** and **2**, we performed DFT calculations (B3LYP/6-31G(d) level).[19] The HOMO–LUMO gap for **2** was calculated to be 1.75 eV and scarce electron density on its two *sp*^{3} carbons was observed in its HOMO and LUMO orbitals. On the other hand, the HOMO–LUMO gap of **1** was calculated to be relatively small 1.33 eV. The π-orbitals derived from the vinylene bridge of **1** was clearly observed in its HOMO and LUMO. The nucleus-independent chemical shift (NICS) values[20] at the center of the macrocycles (NICS(0)) were calculated to be –2.50 ppm for **2** and +19.60 ppm for **1**, supporting nonaromatic and strongly antiaromatic characters for **2** and **1**, respectively. We also calculated the rotational barrier of the vinylene bridge of **1** to be ca. 10.1 kcal/mol. In the optimized structure of transition state (**1-TS**), the bond length of C25–C26 is 1.341 Å and those of adjacent C24–C25 and C26–C1 bonds are 1.467 and 1.465 Å. Therefore, the C25–C26 vinylene group is rotating about C24–C25 and C26–C1 single bonds keeping its character of C25–C26 double bond. (see SI)

In summary, we synthesized [24]pentaphyrin(2.1.1.1.1) **1** as the first example of vinylogous pentaphyrin via dehydrogenation of nonconjugated dihydropentaphyrin(2.1.1.1.1) **2**. Pentaphyrin **1** was certainly stable under ambient conditions despite its strongly antiaromatic character and relatively small conjugation circuit. Further exploration of vinylogous expanded porphyrins bearing *meso*-aryl and *β*-alkyl substituents is now ongoing in our laboratory.

EXPERIMENTAL SECTION

Materials and Methods. All reagents were of the commercial grade and were used without further purification except where noted. The spectroscopic grade dichloromethane was used as a solvent for all spectroscopic studies. Silica gel column chromatography was performed on Wakogel C-200. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck 5554). UV/Visible absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. ^{1}H and ^{19}F NMR spectra were recorded on a JEOL ECZ-400 spectrometer (operating as 399.78 MHz for ^{1}H, 376.13 MHz for ^{19}F, and 100.53 MHz for ^{13}C) using tetramethylsilane(TMS) as the internal reference for ^{1}H and ^{13}C ($\delta = 0$ ppm). Hexafluorobenzene for ^{19}F ($\delta = -162.9$ ppm) was employed as external references. High-resolution electrospray-ionization time-of-flight mass spectroscopy (HR-ESI-TOF-MS) was recorded on a JEOL AccuTOF model using positive mode for methanol solutions of samples. Data for single crystal X-ray diffraction analyses were collected on a Rigaku R-AXIS RAPID diffractometer using a graphite monochromator with CuK_α radiation ($\lambda = 1.54187$ Å). Data collection and reduction were performed using *RAPID AUTO*. The structures for crystallography were solved by direct methods using *SHELXL97*, and were refined using *SHELXL97* on *Yadokari-XG* program.

11,16,21,26-tetrakis(pentafluorophenyl)-3,8-bis(ethoxycarbonyl)-2,9-dimethyl 5,6-dihydropentaphyrin(2.1.1.1.1) 2. 5,10-bis(pentafluorophenyl)-1,14-bis(pentafluorobenzoyl)tripyrrane **A** (940 mg, 1.0 mmol) was reduced with $NaBH_4$ (378 mg, 20 eq) in a 10:1 mixture solution of THF and methanol (110 mL). After 1 h, the reaction was quenched with water and the products were extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield di-carbinol **B** quantitatively, which was unstable at ambient temperature and hence had to be used immediately. The di-carbinol was added to a solution of 1,2-bis(3-ethoxycarbonyl-4-methylpyrrol-2-yl)ethane **C** (341 mg, 1.0 mmol) in CH_2Cl_2 (200 mL). After the resultant solution was stirred in N_2 atmosphere for 5 min, *p*-toluenesulfonic acid monohydrate (57.6 mg, 0.30 eq) was added and stirring was continued for 1.5 h. DDQ (454 mg, 2.0 eq) was added and the resulting solution was stirred for further 5 min. The reaction mixture with 100 mL of ethyl acetate was passed through a basic alumina column with followed by evaporation of solvent under reduced pressure. The residue was purified by silica gel chromatography using 1:10 mixture of EtOAc/Hexane. After collection of the brown band, recrystallization with hexane afforded pure **2**, (118 mg, 0.033 mmol, 10%). ^{1}H NMR($CDCl_3$, 298 K) δ (ppm) = 11.96(brs, 2H, inner NH), 7.12(brs, 1H, outer NH), 6.82(d, J = 4.8 Hz, 2H, β-H), 6.73(s, 2H, β-H), 6.55(d, J = 4.8 Hz, 2H, β-H), 4.39(q, J = 6.8 Hz, 4H, -OCH_2CH$_3$), 2.87(s, 4H, ethylene), 2.11(s, 6H, β-CH_3), 1.36(t, J = 6.8 Hz, 6H, -OCH$_2$$CH_3$): ^{19}F NMR($CDCl_3$, 298 K) δ (ppm) = −137.01(d, J = 18.0 Hz, 4F, *o*-F), −140.05(d, J = 18.0 Hz, 4F, *o*-F), −152.18(d, J = 20.9 Hz, 2F, *p*-F), −152.86(d, J = 20.9 Hz, 2F, *p*-F), −164.26(t, J = 17.9 Hz, 2F, *m*-F), −164.87(t, J = 17.9 Hz, 2F, *m*-F): ^{13}C NMR($CDCl_3$, 298 K) δ (ppm) = 164.9, 159.2, 154.1, 148.3, 146.5, 137.4, 131.5, 130.8, 130.7, 124.2, 118.6, 118.1, 98.4, 60.3, 29.3, 14.4, 12.3 (The signals for *meso*-pentafluorophenyl carbons were not observed clearly because of their complicated ^{13}C-F coupling); UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε[$M^{-1}cm^{-1}$])= 385(36000), 433(46000), 508(11600), and 787(34000). HRMS(ESI-TOF, positive mode) *m/z* $[M+H]^+$ Calced for $C_{58}H_{30}F_{20}N_5O_4^+$ 1240.1973; Found 1240.1948.

11,16,21,26-tetrakis(pentafluorophenyl)-3,8-bis(ethoxycarbonyl)-2,9-dimethyl pentaphyrin(2.1.1.1.1) 1. Dihydropentaphyrin **2** (37.2 mg, 0.30 mmol) was stirred with chloranil (73.8 mg, 10 eq) in toluene (6 mL) at 120 °C. After 12 h, the reaction mixture was extracted with ethyl acetate and washed five times with saturated $NaHCO_3$ solution. The organic phase was washed again with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to dryness under reduced pressure. The residue was dissolved again to CH_2Cl_2 and passed through a short silica-gel column followed by evaporation of solvent under reduced pressure. Recrystallization with hexane gave pure [24]pentaphyrin(2.1.1.1.1) **1** (28.8 mg, 0.23 mmol, 78%). ^{1}H NMR ($CDCl_3$, 298 K): δ (ppm) = 26.11(brs, 2H, inner NH), 17.68(s, 2H, inner β-H), 11.57(s, 2H, -CH=CH-), 4.48(d, J = 4.4 Hz, 2H, outer β-H), 4.04 (d, J = 4.4 Hz, 2H, outer β-H), 3.77(q, J = 6.8 Hz, 4H, -OCH_2CH$_3$) 2.86(s, 1H, outer NH), 1.56(s, 6H, β-CH_3), 1.00(t, J = 6.8 Hz, 6H, -OCH$_2$$CH_3$); ^{19}F NMR($CDCl_3$, 298 K): δ (ppm) = −135.58(d, J = 18.1 Hz, 4F, *o*-F), −140.88(d, J = 17.7 Hz, 4F, *o*-F), −152.90(t, J = 24.1 Hz, 2F, *p*-F), −153.00(t, J = 17.7 Hz, 2F, *p*-F), 160.9-−161.2(m, 8F, *m*-F) ^{13}C NMR($CDCl_3$, 298 K) δ (ppm) = 165.7, 163.1, 153.2, 151.1, 150.7, 138.7, 139.3, 138.5, 136.7, 130.5, 127.1, 123.4, 121.9, 121.5, 60.1, 13.9, 10.2 (The signals for *meso*-pentafluorophenyl carbons were not observed clearly because of their complicated ^{13}C-F coupling);. UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [$M^{-1}cm^{-1}$]) = 498(63000) and 1050(1000). HRMS(ESI-TOF, negative mode): *m/z*: $[M-H]^-$, Calcd for $C_{58}H_{26}F_{20}N_5O_4^-$ 1236.1671; Found 1236.1697.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

X-ray crystallographic data for compound **1** and **2** (CIF)

^{1}H, ^{19}F and ^{13}C NMR spectra of compounds; Cyclic voltammograms; detailed X-Ray crystallographic data; and calculated data (PDF)

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Notes

The authors declare no competing financial interest.

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(16) Crystal data for **2**, $C_{58}H_{29}F_{20}N_5O_4\cdot 3$(acetonitrile) ($M$r=1363.03), Monoclinic, space group $P2_1/n$ (No. 14), a = 22.5153(9), b = 8.3136(3), c = 32.1163(13) Å, β = 100.0015(18), V = 5901.1(4) Å^3, Z = 4, ρ_{calcd} = 1.534 gcm^{-3}, T = 93(2) K, R_1 = 0.0736 (I >2σ(I)), wR_2= 0.2176 (all data), GOF = 0.997. CCDC = 1552260.

(17) Crystal data for **1**, 2($C_{58}H_{27}F_{20}N_5O_4$)·2(nonane)·(water) (Mr=2748.20), Triclinic, space group P-1 (No. 2), a = 15.9571(9), b = 18.4976(11), c = 21.6413(11) Å, α = 80.425(5), β = 84.180(4), γ = 83.638(5), V = 6237.6(6) Å^3, Z = 2, ρ_{calcd}= 1.463 gcm^{-3}, T = 93(2) K, R_1= 0.1109 (I >2σ(I)), wR_2= 0.3419 (all data), GOF = 1.066, CCDC = 1552261.

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