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meso-Trifluoromethyl-Substituted Expanded Porphyrins

Soji Shimizu, Naoki Aratani, and Atsuhiro Osuka*[a]

Abstract: A series of *meso*-trifluoromethyl-substituted expanded porphyrins, including N-fused [24]pentaphyrin **3**, [28]hexaphyrin **4**, [32]heptaphyrin **5**, [46]decaphyrin **6**, and [56]dodecaphyrin **7**, were synthesized by means of an acid-catalyzed one-pot condensation reaction of 2-(2,2,2-trifluoro-1-hydroxyethyl)pyrrole (**1**) as the first examples bearing *meso*-alkyl substituents. Besides these products, porphyrin **2** and two calix[5]phyrins **8** and **9** were also obtained. [28]Hexaphyrin **4** was quantitatively oxidized to [26]hexaphyrin **14** with MnO_2. These expanded porphyrins have been characterized by mass spectrometry, ^1H and ^{19}F NMR spectroscopy, and UV/Vis spectroscopy. The single-crystal structures have been determined for **3**, **4**, **6**, **7**, and **14**. The N-fused [24]pentaphyrin **3** displays a distorted structure containing a tricyclic fused moiety that is similar to those of *meso*-aryl-substituted counterparts, whereas **8** and **9** are indicated to take roughly planar conformations with an inverted pyrrole opposite to the sp^3-hybridized *meso*-carbon atom. Both [28]- and [26]hexaphyrins **4** and **14** have figure-of-eight structures. Solid-state structures of the decaphyrin **6** and dodecaphyrin **7** are remarkable, exhibiting a crescent conformation and an intramolecular two-pitch helical conformation, respectively.

Keywords: aromaticity · conjugation · macrocyclic ligands · porphyrinoids

Introduction

Expanded porphyrins[1] are emerging functional molecules in light of their potential utilities in a range of applications, such as anion receptors,[2] transition or lanthanoid ion chelates,[3] photodynamic therapy sensitizers,[4] and magnetic resonance imaging (MRI) contrast agents.[5] In addition, their large two-photon absorption cross sections have been recently revealed as promising attributes for their uses in three-dimensional microfabrication, optical data storage, and optical limiting.[6] These fascinating properties have encouraged synthetic efforts towards a variety of expanded porphyrins differing in ring size, ring connectivity, peripheral substituent, and core modification. As a consequence, many carefully designed expanded porphyrins have been developed in recent years,[1,7–14] but *homologous expanded porphyrins* that consist of more than four pyrrolic units with the regular alternate arrangement of pyrrole groups and methine carbon atoms still remain rather limited. Although such expanded porphyrins may be formed along with a porphyrin by one-pot condensation of pyrrole and aldehyde, only three reactions have been reported that are effective for the synthesis of homologous expanded porphyrins; 1) the reaction of pyrrole with 2,6-disubstituted benzaldehyde,[15a] 2) the reaction of 3,4-difluoropyrrole with pentafluorobenzaldehyde,[15b] and 3) the reaction of 3,4-diethylpyrrole with triisopropylsilylpropynal.[16] These expanded porphyrins allow systematic investigations on the optical, electrochemical, and coordination properties upon change in number of pyrrolic units, for which *meso*-substituents are expected to play a profound impact.

With this background, we wished to prepare *meso*-alkyl-substituted homologous expanded porphyrins. In our syntheses of *meso*-aryl-substituted expanded porphyrins, the use of aromatic aldehydes that bear electron-deficient substituents at 2- and 6-positions is crucial,[15] since 2-halobenzaldehyde, 2,4-dihalobenzaldehyde, or 2,6-dimethylbenzaldehyde failed to give expanded porphyrins under similar conditions. These results imply that the presence of bulky substituents at the *meso*-positions in porphyrinogen precursors may shift an acid-formed equilibrated mixture favorably toward cyclic ex-

[a] S. Shimizu, Dr. N. Aratani, Prof. A. Osuka
Department of Chemistry
Graduate School of Science, Kyoto University
and
Core Research for Evolutional Science and Technology (CREST)
Japan Science and Technology Agency, Sakyo-ku
Kyoto 606–8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp

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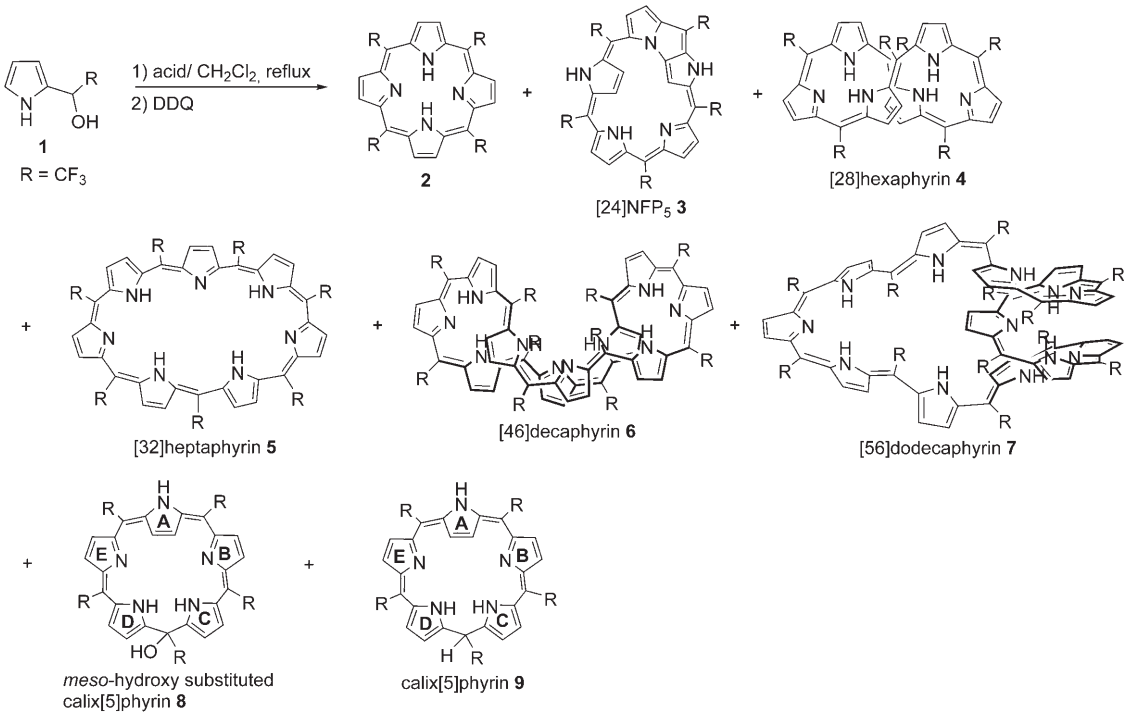
panded porphyrinogens, or the electron-deficient substituents either on aromatic aldehyde or pyrrole may tend to stabilize such precursors. This consideration drove us to examine the synthesis of *meso*-trifluoromethyl-substituted expanded porphyrins. A trifluoromethyl group is sufficiently electron-deficient and certainly sterically demanding, which may meet the above synthetic requirements. In this paper, the syntheses of *meso*-trifluoromethyl-substituted expanded porphyrins are described as the first examples bearing *meso*-alkyl substituents;[17] 2-(2,2,2-trifluoro-1-hydroxyethyl)pyrrole (**1**) or 2-(2,2,2-trifluoro-1-hydroxyethyl)-6-trifluoromethyldipyrromethane (**11**) were successfully employed as key precursors. Expanded porphyrins reported in this paper are named partly based on the nomenclature put forward by Franck and Nonn for porphyrinoids.[1h,i]

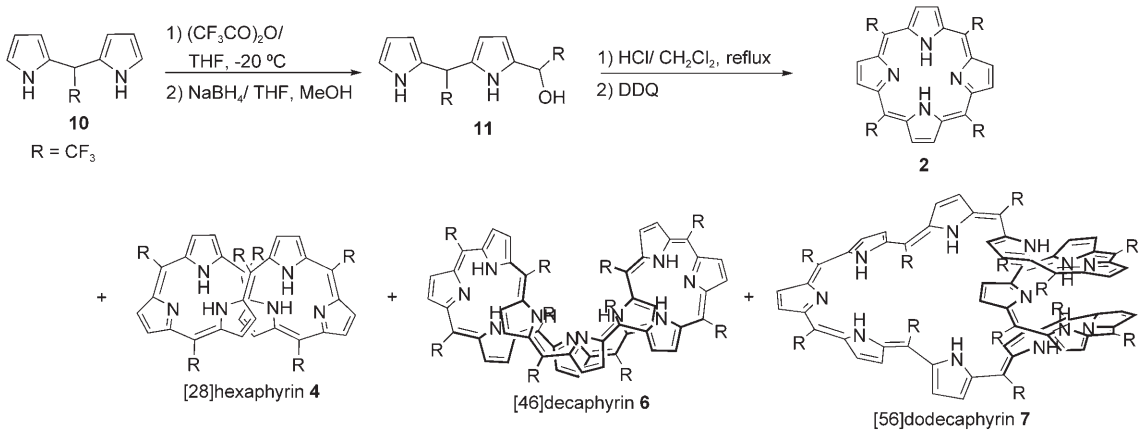
Results and Discussion

Syntheses: 2-(2,2,2-Trifluoro-1-hydroxyethyl)pyrrole (**1**) was prepared from acylation reaction of pyrrole with trifluoroacetic anhydride (TFAA) in benzene at 0 °C, followed by reduction with $NaBH_4$ in THF/MeOH.[18] After acid-catalyzed cyclization reactions of **1** had been examined for the synthesis of expanded porphyrins under various reaction conditions, we found the reaction conditions that allowed the synthesis of a series of *meso*-trifluoromethyl-substituted expanded porphyrins in small but reproducible yields. A solution of **1** (66.6 mM) in CH_2Cl_2 was refluxed with an equivalent amount of HCl (1.0 M in diethyl ether) for 12 h. After oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 2.3 equiv) for 6 h at room temperature, the reaction mixture was separated by repeated chromatography over silica gel and gel permeation chromatography (GPC) columns to give *meso*-trifluoromethyl-substituted expanded porphyrins (porphyrin **2** (2–3%), N-fused pentaphyrin **3** (5–10%), hexaphyrin **4** (3–4%), heptaphyrin **5** (4–6%), decaphyrin **6** (~1%), and dodecaphyrin **7** (~1%), Scheme 1).[19] In addition to these fully conjugated expanded porphyrins, *meso*-hydroxy-substituted calix[5]phyrin **8** was also obtained in 4% yield. Methanesulfonic acid (MSA) was found to be also effective for this reaction. With a catalytic amount of MSA (0.4 equiv)[20] under the similar conditions, the reaction gave **2**, **3**, **4**, **5**, **6**, **7**, and **8** in 2, 2, 2, 6, ~1, ~1, and 4% yields, respectively, along with another calix[5]phyrin **9** in 2% yield.

Ring-size selective syntheses[21] of *meso*-trifluoromethyl-substituted expanded porphyrins have been explored by using oligopyrrolic precursors **11**, **12**, and **13** (Schemes 2 and 3). *meso*-Trifluoromethyl-substituted dipyrromethane[22] **10** was treated with four equivalents of TFAA in THF at −20 °C to give 2-trifluoroacetyl-6-trifluoromethyldipyrromethane in 82–88% yield, which was quantitatively reduced with $NaBH_4$ to its carbinol **11**. Self-condensation reaction of **11** with one equivalent of HCl in refluxing CH_2Cl_2 provided a series of *meso*-trifluoromethyl-substituted expanded porphyrins bearing an even number of regularly arranged pyrrole rings and methine carbon atoms (**2** 1–3%, **4** 8–10%, **6** ~1%, and **7** ~1%, Scheme 2). When treated with excess pyrrole (11 equiv) and HCl (0.9 equiv) in THF under refluxing conditions for 4 h, the dipyrromethane derivative **11** was converted to *meso*-trifluoromethyl-substituted tripyrrometh-



Scheme 1. Synthesis of a series of *meso*-trifluoromethyl-substituted expanded porphyrins.



Scheme 2. Ring-size selective synthesis from **11**.

ane **12** in 56% yield.[18] Even under temperature-controlled conditions similar to monoacylation of **10**, the tripyrromethane **12** gave a mixture of mono- and diacylated tripyrromethane that was hard to separate. Diacylation reaction of **10** with an excess amount of TFAA in toluene at room temperature quantitatively afforded 2,2′-bis(trifluoroacetyl)-6-trifluoromethyldipyrromethane, which was then reduced to dipyrromethane dicarbinol **13**. A condensation reaction of **12** and **13** with 0.5 equivalents of MSA gave **3**, **8**, and **9** in 1–2%, ~1.5%, and 4–5% yields, respectively (Scheme 3), while the reaction with one equivalent of HCl gave **9** in a better yield (5–7%).

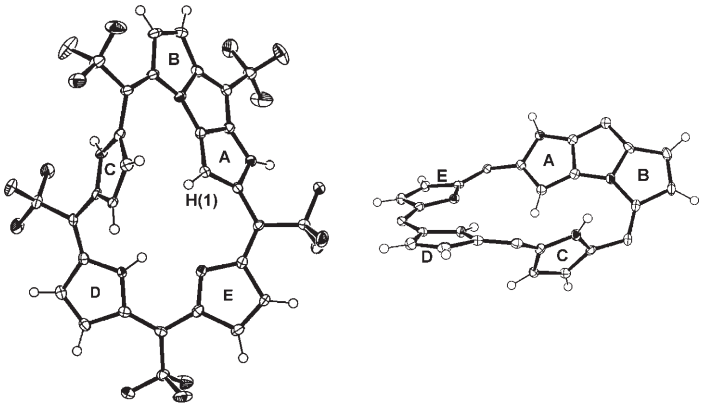
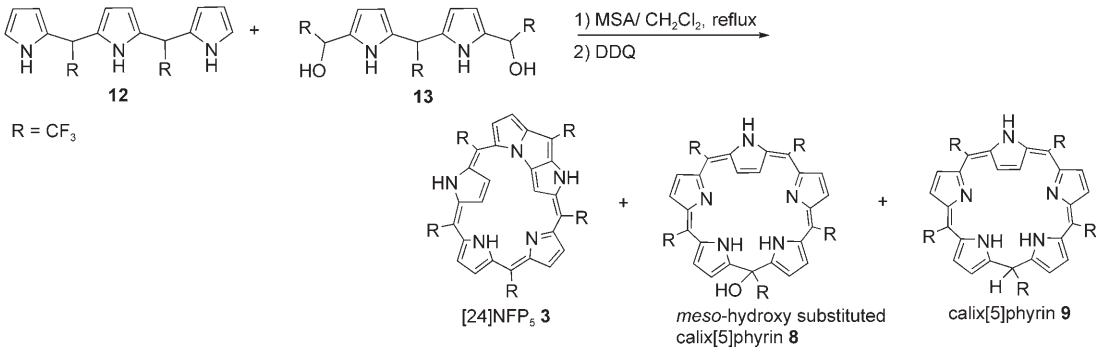


Figure 1. X-ray crystal structure of **3**, top view (left) and side view (right). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Trifluoromethyl substituents are omitted in the side view for clarity.

Structural characterization of N-fused [24]pentaphyrin 3: High-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectroscopy revealed the parent ion peak of **3** at 726.0771 ($[M-H]^-$, calcd for $C_{30}N_5F_{15}H_{11}$, 726.0780). X-ray diffraction analysis has unambiguously revealed a distorted N-fused pentaphyrin (NFP_5) structure of **3** (Figure 1), in which the nitrogen atom of the pyrrole B is attached at the β-position of the pyrrole A to form a fused tricyclic segment and the pyrroles A, C, and D possess NH hydrogen atoms, thus indicating its formulation as a [24]NFP_5. The tilting angles of the pyrroles from the macrocyclic mean-plane defined by 30 core atoms are large; 18.6° (pyrrole E), 25.6° (pyrrole D), and 76.8° (pyrrole C). Thus, the entire structure is quite distorted, being unfavorable for overall macrocyclic conjugation. Reflecting this structural feature, the ^{1}H NMR spectrum of **3** in CD_2Cl_2 at room temperature contained three NH proton signals at $\delta = 9.26$, 8.62, and 8.05 ppm and nine β-CH protons resonated at $\delta = 7.80$, 7.63–7.59 (2H), 7.52, 7.28, 7.12, 6.43, 5.95, and 3.09 ppm. These data indicate the nonaromatic character of **3** in contrast to the antiaromaticity of *meso*-aryl-substituted [24]NFP_5.[23,24] The most up-



Scheme 3. Ring-size selective synthesis from **12** and **13**.

field shifted peak at $\delta = 3.09$ ppm has been assigned to the inner β-CH proton of the pyrrole A (H(1) in Figure 1), which exhibits correlation with the outer NH at $\delta =$ 8.62 ppm in the H-H COSY spectrum. Hence, the large upfield shift of H(1) may be ascribed to the local diatropic ring current effect of the pyrrole C, which is close to H(1) with a distance of 2.57 Å. In contrast to the quantitative and reversible redox interconversions between [24]- and [22]NFP_5[23,24] bearing *meso*-pentafluorophenyl substituents, oxidation of **3** to its [22]NFP_5 counterpart was found to be difficult even with DDQ or MnO_2 under forcing conditions.

Structural characterization of calix[5]phyrins 8 and 9: The HR-ESI-TOF mass spectra of **8** and **9** exhibited the parent ion peaks at 744.0855 and 728.0913, respectively ($[M-H]^-$; calcd for $C_{30}N_5F_{15}H_{13}O$ for **8**, 744.0886 and $C_{30}N_5F_{15}H_{13}$ for **9**, 728.0937) in line with the assigned calix[5]phyrin structures bearing a hydroxyl group and a hydrogen atom at the saturated sp^3-hybridized *meso*-carbon atom, respectively, as shown in Scheme 1. Preliminary single-crystal structures were obtained for both compounds, which revealed that the pyrrole ring A is pointing outward and the other are orienting inward with three NH hydrogen atoms at the pyrroles A, C, and D (Scheme 1 and see Supporting information). The ^1H NMR spectrum of **8** in $CDCl_3$ exhibited two signals due to the NH protons at $\delta = 10.02$ and 9.22 ppm in a 2:1 ratio; four signals due to the β-CH protons at $\delta = 7.84$, 7.55, 7.42, and 4.94 ppm in a 2:1:1:1 ratio; and one singlet due to the *meso*-OH proton at $\delta = 2.23$ ppm. Similarly, the ^1H NMR spectrum of **9** in $CDCl_3$ showed two signals due to NH protons at $\delta = 10.81$ and 9.19 ppm in a 2:1 ratio; five peaks due to the β-CH protons at $\delta = 7.74$, 7.73, 7.45, 7.34, and 5.26 ppm in a 1:1:1:1:1 ratio; and a quartet peak due to the sp^3-*meso*-CH proton at $\delta = 2.64$ ppm, which is coupled with the fluorine atoms of the *meso*-trifluoromethyl substituent. The ^{19}F NMR spectra of **8** and **9** in $CDCl_3$ showed three peaks in a 2:2:1 ratio at $\delta = -53.65$, -55.59, and -82.85 ppm and at $\delta = -52.79$, -54.59, and -70.16 ppm, respectively. The ^{13}C NMR spectrum of **9** showed peaks between $\delta = 100$ and 150 ppm, except for one peak at $\delta = 47.4$ ppm that correlated with the proton peak at $\delta = 2.64$ ppm in the H-C COSY spectrum, while the ^{13}C NMR spectrum of **8** exhibited most peaks between $\delta = 100$ and 150 ppm and one peak at $\delta = 73.4$ ppm. These NMR spectra supported the preliminary crystal structures. Since **8** and **9** can be classified as analogues of calixphyrin, we named them as calix[5]phyrin for **8** and **9**.[25] These macrocycles are, to the best of our knowledge, the first calix[5]phyrin-type molecules with homologous pentaphyrin frameworks. Plausibly, the formation of **9** may be caused by sterically bulky *meso*-trifluoromethyl substituents that retard full oxidation of a pentaphyrinogen precursor.

Structural characterization of [28]hexaphyrin 4 and [26]hexaphyrin 14: The HR-ESI-TOF mass spectrum of **4** showed its parent ion peak at 873.1064 ($[M-H]^-$; calcd for $C_{36}N_6F_{18}H_{15}$: 873.1076). The X-ray diffraction analysis revealed a twisted figure-of-eight conformation of **4** consisting of two oblique near planar tripyrrolic hemimacrocycles held with a dihedral angle of 66° (Figure 2). These hemimacrocycles are both helically wound with the aid of mutual hydrogen-bonding interactions between the amine and imine moieties of the pyrroles A, B, and C, and D, E, and F with N–H···N distances and angles of 2.07 Å and 124° (A to B), 1.94 Å and 134° (B to C), 2.33 Å and 108° (D to E), and 2.00 Å and 131° (E to F), respectively. The structure of **4** is similar to that of perfluorinated [28]hexaphyrin[15b] with respect to the helical structure as well as the presence of four NH hydrogen atoms, which leads to the assignment of **4** as a [28]hexaphyrin. In accord with this structural assignment, the ^1H NMR spectrum of **4** in CD_2Cl_2 at room temperature has two peaks due to the NH protons at $\delta = 14.95$ and 12.35 ppm and broad peaks due to the β-CH protons between $\delta = 7.37$ and 6.88 ppm, which became six well-resolved peaks at $\delta = 7.43$, 7.23, 7.00, 6.95, 6.90, and 6.77 ppm at −80 °C. The ^{19}F NMR spectrum exhibited three peaks at $\delta = -55.40$, -56.65, and -57.51 ppm at −80 °C, reflecting a C_2 symmetric structure of **4**.

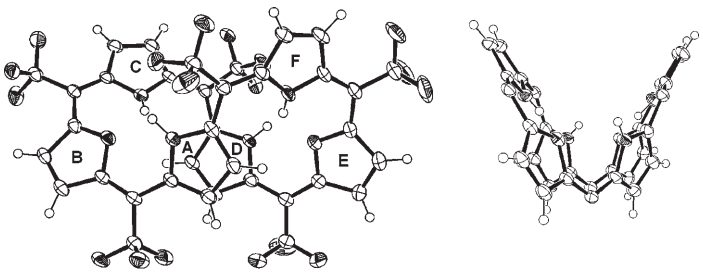
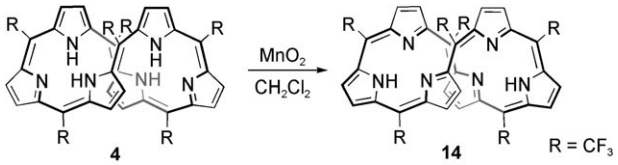


Figure 2. X-ray crystal structure of **4**, top view (left) and side view (right). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Trifluoromethyl substituents are omitted in the side view for clarity.

The hexaphyrin **4** was found not to oxidize while stored under ambient conditions, but was smoothly oxidized with MnO_2 to give [26]hexaphyrin **14** quantitatively (Scheme 4).



Scheme 4. Oxidation of **4** to **14**.

HR-ESI-TOF mass spectrum of **14** exhibited molecular ion peak at 873.1061 ($[M+H]^+$; calcd for $C_{36}N_6F_{18}H_{15}$: 873.1065), which confirmed the loss of two hydrogen atoms from **4**. The ^1H NMR spectrum exhibited six peaks due to the β-CH protons at $\delta = 7.88$, 7.67, 7.54, 7.38, 6.33, and 5.99 ppm and one peak due to the NH protons at $\delta =$

11.11 ppm, which disappeared upon the addition of D_2O. These results indicate that there is no strong diatropic ring current in **14**, despite its cyclic 26π-electron conjugation. Finally the structure of **14** was determined by X-ray diffraction analysis. Compound **14** exhibits a twisted figure-of-eight structure with two NH hydrogen atoms at the pyrroles B and E (Figure 3), similar to that of **4**. Here it is to be noted

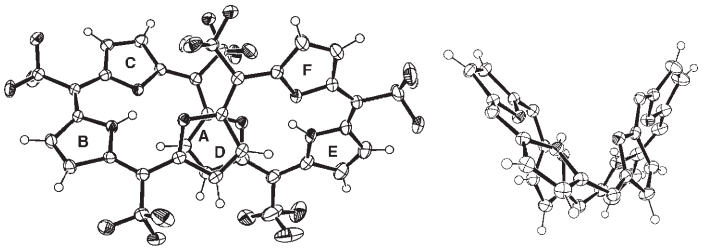


Figure 3. X-ray crystal structure of **14**, top view (left) and side view (right). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Trifluoromethyl substituents are omitted in the side view for clarity.

that the hexaphyrin **14** is, to the best of our knowledge, the first nonaromatic [26]hexaphyrin(1.1.1.1.1.1), which is due to non-planarity of the molecule caused by the substantial steric hindrance.[26]

Structural characterization of [32]heptaphyrin 5: The HR-ESI-TOF mass spectrum of **5** showed its molecular ion peak at 1018.1213 ($[M-H]^-$; calcd for $C_{42}N_7F_{21}H_{17}$: 1018.1216). The ^{1}H NMR spectrum in $CDCl_3$ at room temperature displays two signals at $\delta = 15.68$ and 11.15 ppm due to the NH protons and five signals due to the β-CH protons at $\delta = 9.93$, 8.90, 7.79, 7.56, and 6.60 ppm. The ^{19}F NMR spectrum of **5** exhibited four peaks at $\delta = -50.72$, -51.17, -55.26, and -57.46 ppm in a 2:1:2:2 ratio. Overall these NMR data suggested a C_2 symmetric structure with four NH protons, thus indicating 32π-electronic conjugation for **5**. It is notable that the heptaphyrin **5** is thermally quite stable in a solution, in contrast to *meso*-pentafluorophenyl[32]heptaphyrin[15a] and perfluorinated[32]heptaphyrin,[15b] which are both thermally unstable, being gradually converted to their N-fused heptaphyrins just on standing. The chemical stability of **5** evidently arises from the lack of *meso*-pentafluorophenyl substituents, since the *ortho*-fluorine atoms in the heptaphyrins are susceptible for the nucleophilic substitution reaction of the neighboring pyrrolic nitrogen atom.

Structural characterization of [46]decaphyrin 6: *meso*-Trifluoromethyl-substituted decaphyrin **6** could not be purified by silica-gel column chromatography, because calix[5]phyrin **9** had similar polarity in silica-gel column, but the large difference in molecular size enabled clear separation through gel-permeation chromatography. The HR-ESI-TOF mass spectrum of **6** exhibited the parent ion peak at 1455.1784 ($[M-H]^-$; Calcd for $C_{60}N_{10}F_{30}H_{25}$: 1455.1790). The solid-state structure of **6** was determined by X-ray single crystal diffraction analysis. Compound **6** has a near C_2 symmetric crescent-like conformation consisting of six aminopyrrole rings and four iminopyrrole rings, thus indicating its formulation as a [46]decaphyrin (Figure 4). The structure of **6** con-

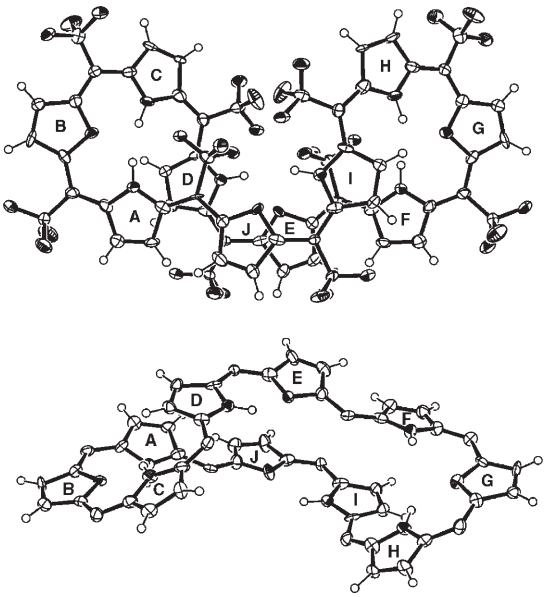


Figure 4. X-ray crystal structure of **6**, top view (top) and side view (bottom). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Trifluoromethyl substituents are omitted in the side view for clarity.

sists of two segments: semihelical tripyrrolic subunits (the pyrroles A, B, and C, and the pyrroles F, G, and H) and near planar dipyrromethene subunits (the pyrroles D and E, and the pyrroles I and J). Both semihelical subunits are held by the aid of hydrogen bonding between the amine NH groups and imine nitrogen atoms of the pyrrole rings. The ^{19}F NMR spectrum of **6** in $CDCl_3$ at room temperature exhibited rather broad two sets of peaks, which became sharp on lowering temperature. At $-60\,^\circ$C, one set of peaks appeared at $\delta = -44.55$, -46.02, -47.04, -47.84, -48.44, -49.39, -54.87, -56.64, and -58.53 ppm in a 2:1:1:1:1:1:1:1:1:1 ratio and the other, which consists of five peaks, appeared at $\delta = -50.93$, -51.97, -52.18, -54.54, and -59.18 ppm, indicating that asymmetric and symmetric conformations (**6-I** and **6-II**, respectively) exist in equilibrium in 1:0.3 ratio in $CDCl_3$ (see the Supporting Information). Variable-temperature ^{1}H NMR measurements were also examined to confirm the existence of two conformations in solution. At $-60\,^\circ$C, the peaks became well-resolved and were assigned to each conformer by H-H COSY experiments to reveal that the twenty peaks due to β-CH protons of **6-I** appeared at $\delta = 8.32$, 8.21, 7.94, 7.84, 7.78, 7.76, 7.67, 7.60, 7.57, 7.41, 7.20–7.19 (2H), 6.74, 6.59, 6.56, 6.49, 6.37, 5.86, 4.83, and 4.30 ppm, and six NH protons resonated at $\delta = 8.16$, 7.14, 5.82, 3.44, 3.35, and 1.08 ppm, while the β-CH peaks of **6-II** were observed at $\delta = 7.73$, 7.60, 7.48, 7.34, 7.31, 7.26, 7.16, 7.13, 6.80, and 6.77 ppm and six NH protons resonated

at $\delta = 12.45$, 10.72, and 10.61 ppm; these results reflect the asymmetric and symmetric nature of **6-I** and **6-II**, respectively. The conformer **6-I** exhibits large up-field shifts for some β-CH protons and NH peaks, which may be accounted for in terms of some diatropic ring current effect arising from 46π-electron conjugation.[27]

Structural characterization of [56]dodecaphyrin 7: The HR-ESI-TOF mass spectrum of **7** exhibited its parent ion peak at 1747.2201 ($[M-H]^-$; Calcd for $C_{72}N_{12}F_{36}H_{31}$: 1747.2225). The solid-state structure of **7** has been revealed by single-crystal X-ray diffraction analysis (Figure 5). Curiously, the

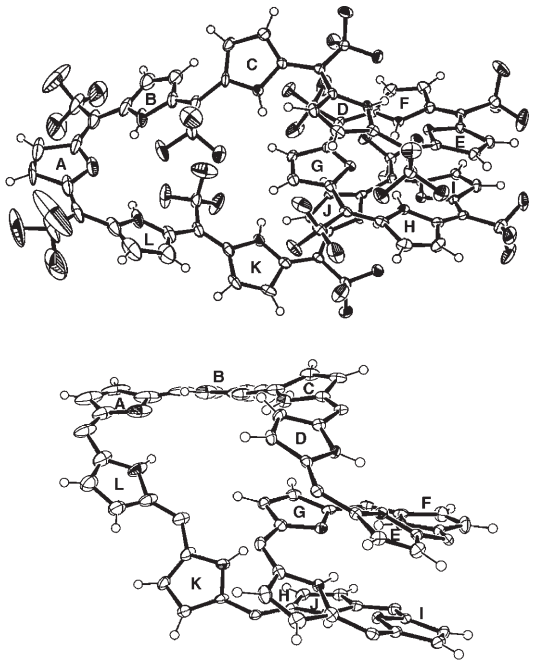


Figure 5. X-ray crystal structure of **7**, top view (top) and side view (bottom). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Trifluoromethyl substituents are omitted in the side view for clarity.

dodecaphyrin macrocycle contains an intramolecularly wound helix, consisting of seven pyrrole rings (the pyrroles D, E, F, G, H, I, and J), that is linked to another semihelix of three pyrrole rings (the pyrroles L, A, and B) through the pyrroles C and K (Figure 5). These two spiral helixes are held with the aid of hydrogen bonding between the amine NH groups and imine nitrogen atoms, in a similar manner as observed in the structures of **4**, **6**, and **14**. The bridging pyrroles C and K possess inward-pointing NH hydrogen atoms, which are used for hydrogen bonding with fluorine atom of the adjacent trifluoromethyl substituents. The helix in **7** can be characterized by a one-pitch distance of ca. 3.6 Å and a diameter of 3.2 Å, while the diameter of semihelix is approximately 3.2 Å. The dodecaphyrin **7** possesses eight NH hydrogen atoms, thus leading to the assignment of **7** as a [56]dodecaphyrin. Similar to the case of **6**, both ^{1}H and ^{19}F NMR spectra at room temperature showed very broad peaks. In the ^{19}F NMR spectrum of **7** in CD_2Cl_2, six broad peaks were observed at room temperature, which became well-resolved peaks at $\delta = -45.00$, −49.34, −51.18, −54.78, −56.33, and −59.47 ppm with twelve smaller peaks at $\delta =$ −44.06, −45.88, −49.50, −50.20, −51.37, −53.39, −53.82, −56.59, −56.75, −56.99, −57.33, and −57.61 ppm at −90 °C, suggesting the existence of symmetric and asymmetric conformers, **7-I** and **7-II**, respectively, in a 1:0.3 ratio (see the Supporting Information). In agreement with this consideration, the ^{1}H NMR spectrum exhibited the NH proton peaks due to the major conformer **7-I** at $\delta = 12.80$, 9.40, 8.23, and 6.31 ppm, and its β-CH protons appeared at $\delta = 8.92$, 8.35, 7.74, 7.32, 7.13, 7.04–6.98, 6.78, 6.74, and 6.46 ppm, while the peaks due to the minor asymmetrical conformer **7-II** were hard to assign at −90 °C (see the Supporting Information). To the best of our knowledge, **7** is the largest structurally well-characterized expanded porphyrin formed from a one-pot condensation of a monopyrrolic substrate.

UV/Vis absorption spectra: Absorption spectra of expanded porphyrins are known to shift to the lower energy side as the ring-size (conjugation) becomes larger. The same trend is observed for the present series. Figure 6 shows absorption spectra of various *meso*-trifluoromethyl-substituted expanded porphyrins taken in CH_2Cl_2. The N-fused pentaphyrin **3** has a broad band at 472 nm and a less intense broad absorption at 643 nm, both of which are blue-shifted relative to those of *meso*-pentafluorophenyl-substituted [24]NFP_5 (Figure 6b).[23,24] The absorption spectra of the calix[5]phyrins **8** and **9** are similar to each other, exhibiting a broad absorption band at 481 nm and a weak absorption band at 673 nm for **8** and those at 466 and 663 nm for **9** (Figure 6c and d). These spectra are also analogous to that of **3** in respect of shape and position, but their absorption coefficients are larger than that of **3**. The [28]hexaphyrin **4** exhibits a split absorption band at 506 and 557 nm without any low energy bands (Figure 6e), while the [26]hexaphyrin **14** exhibits a much sharper and intense absorption band at 581 nm with a broad weaker band at 748 nm (Figure 6f). The heptaphyrin **5** displays two broad absorption bands at 572 and 363 nm (Figure 6g), which are similar to those of *meso*-pentafluorophenyl-substituted [32]heptaphyrin[15a] and perfluorinated [32]heptaphyrin.[15b] The absorption spectrum **6** shows three broad bands at 447, 746, and 1036 nm (Figure 6h). It is interesting to note that the lowest energy band reaches into near-IR region, probably reflecting its extensive π conjugation. Finally, the absorption spectrum of **7** shows three broad bands at 397, 532, and 778 nm, with a very broad band tailing up to 1500 nm (Figure 6i).

Conclusion

meso-Trifluoromethyl-substituted expanded porphyrins **3**, **4**, **5**, **6**, **7**, **8**, and **9** were synthesized as the first examples bearing *meso*-alkyl substituents. *meso*-Trifluoromethyl substituents exert a large influence on the structures and stabilities

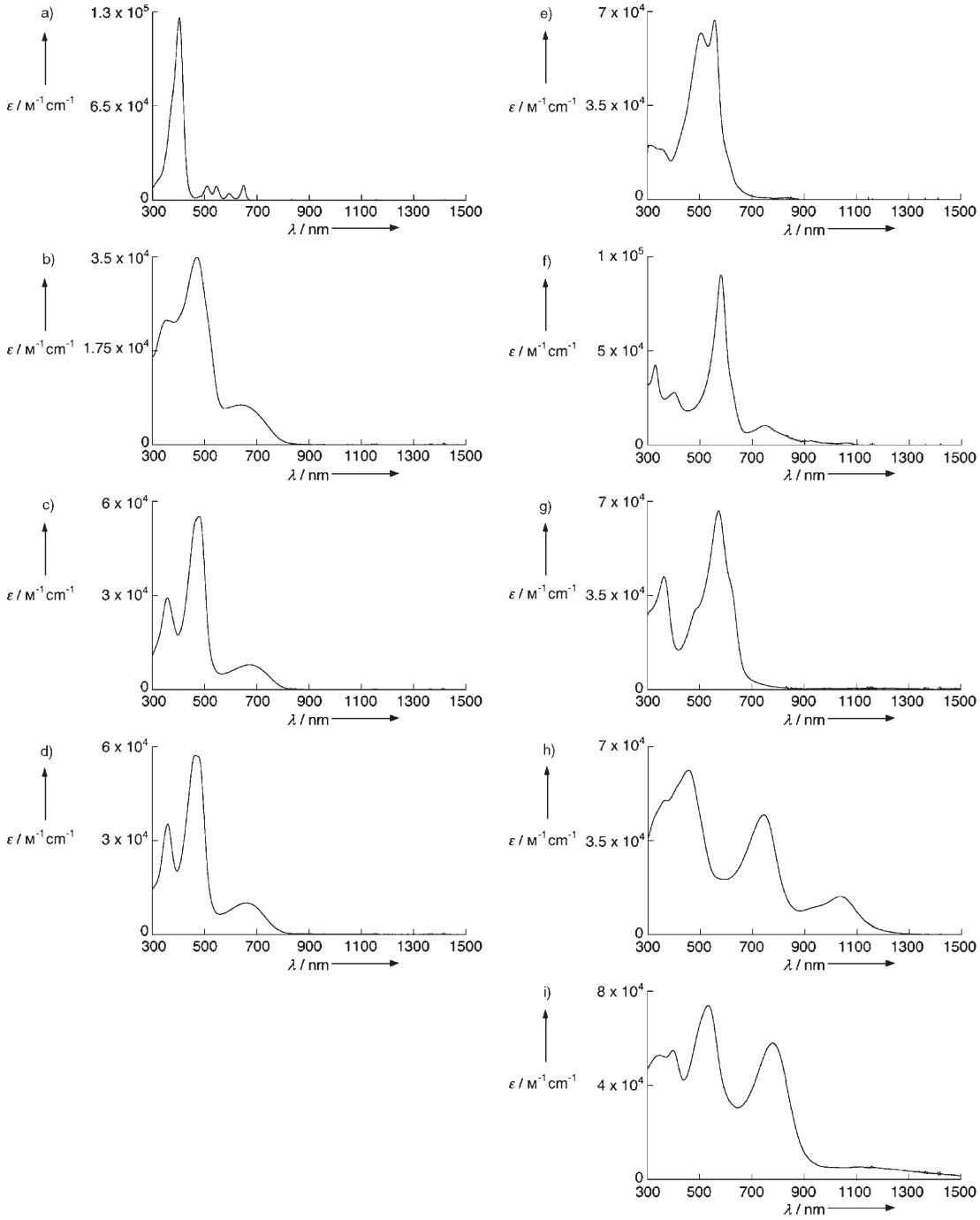


Figure 6. UV/Vis absorption spectra of a) **2**, b) **3**, c) **8**, d) **9**, e) **4**, f) **14**, g) **5**, h) **6**, and i) **7**.

of the expanded porphyrins; this influence can clearly been seen in that the pentapyrrolic macrocycles **8** and **9** were isolated as calix[5]phyins for the first time, both [28]- and [26]hexaphyrins **4** and **14** take figure-of-eight conformations, the heptaphyrin **5** is chemically quite stable, and crescent and partial helical structures have been revealed for decaphyrin **6** and dodecaphyrin **7**. These expanded porphyrins are expected to have different properties from those of the normal expanded porphyrins, particularly in multiple coordination of metal ions, which will be an attractive next target. Investigations along this direction are now currently in progress in our laboratory.

Experimental Section

General procedure: All reagents and solvents were of the commercial reagent grade and were used without further purification except where

noted. Dry CH_2Cl_2 was obtained by distilling over CaH_2. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600.17 MHz for ^1H, 150.91 MHz for ^{13}C, and 564.73 MHz for ^{19}F) using the residual solvent as the internal reference for ^1H ($\delta =$ 7.260 ppm for $CDCl_3$ and $\delta = 5.320$ ppm for CD_2Cl_2), and ^{13}C ($\delta =$ 77.0 ppm for $CDCl_3$) and hexafluorobenzene as an external reference for ^{19}F ($\delta = -162.9$ ppm). Spectroscopic grade CH_2Cl_2 was used as the solvent for all spectroscopic studies. UV/Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a JEOL HX-110 spectrometer using positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix, or on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer by using positive-MALDI ionization method. ESI-TOF-MS spectra were recorded on a BRUKER microTOF by using positive- and negative-ion modes and acetonitrile as a solvent. Preparative separations were performed by silica-gel flash column chromatography (Merck Kieselgel 60H Art. 7736), silica-gel gravity column chromatography (Wako gel C-400), or recycling preparative GPC-HPLC that was carried out on JAI LC-908 using preparative JAIGEL-2 H, 2.5 H, and 3H columns.

Crystallographic data collection and structure refinement: Data collection for the compounds **4** and **6** were carried out at -150 °C on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Data collection for the compounds **3**, **7**, and **14** were carried out at -153 °C for **3** and **7** and at -183 °C for **14** on a Bruker SMART APEX diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Details of the crystallographic data are listed in Table 1. The structures were solved by direct methods (Sir 97[28] or SHELXS-97[29]) and refined with Rigaku CrystalStructure software or with full-matrix least square technique (SHELXL-97).[29]

CCDC-296241 (**3**), CCDC-296243 (**4**), CCDC-296244 (**6**), CCDC-296245 (**7**), and CCDC-296242 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of *meso*-trifluoromethyl-substituted expanded porphyrins: In a 100 mL round-bottomed flask under nitrogen 2-(2,2,2-trifluoro-1-hydroxyethyl)pyrrole **1** (0.413 g, 2.5 mmol) was dissolved in dichloromethane (37.5 mL) and was refluxed with HCl in diethyl ether (1.0 M; 2.5 mL purchased from Aldrich) for 12 h. After addition of DDQ (1.28 g, 5.7 mmol), the solution was stirred for an additional 6 h at room temperature. The resulting solution was washed with a saturated aqueous $NaHCO_3$ solution and water. After being dried over Na_2SO_4, the mixture was separated by silica-gel column chromatography and gel-permeation chromatography to afford **2** (2–3%), **3** (5–10%), **4** (3–4%), **5** (4–6%), **6** (~1%), **7** (~1%), and **8** (4%).

Preparation of 2-(2,2,2-trifluoro-1-hydroxyethyl)-6-trifluoromethyldipyrromethane 11: Trifluoroacetic anhydride (10.3 mL, 4.0 equiv) was added to a solution of *meso*-trifluoromethyl-substituted dipyrromethane **10** (4.0 g, 18.7 mmol) in THF (186 mL) cooled at -20 °C, and then the mixture was stirred for 12 h. The reaction mixture was poured into aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. After removal of the solvent, the residue was subjected to distillation through a glass tube oven at 160–180 °C under high vacuum to give pure monoacylated compound as yellow oil in 82–88% yield. The acylated dipyrromethane was reduced with $NaBH_4$ in a mixture of THF and methanol to give **11**.

Synthesis of *meso*-trifluoromethyl-substituted expanded porphyrins from 11: HCl in diethyl ether (1.0 M; 1.58 mL, 1.0 equiv) was added to a solution of **11** (492 mg, 1.58 mmol) in dichloromethane(24 mL), and the mixture was then refluxed for 12 h. After cooling to room temperature, DDQ (807 mg, 3.57 mmol) was added and the reaction mixture was stirred for 6 h. The reaction mixture was neutralized by washing with aqueous $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent, the mixture was separated into each fractions to give **2**, **4**, **6**, and **7** in 1–3%, 8–10%, ~1%, and ~1% yields, respectively.

Preparation of *meso*-trifluoromethyl substituted tripyrromethane 12: Pyrrole (6.0 mL, 10.8 equiv) and HCl (0.6 mL, 0.9 equiv) were added to a solution of **11** (2.5 g, 8.0 mmol) in THF (40 mL), and the resulting mixture was refluxed for 4 h. The reaction mixture was poured into aqueous $NaHCO_3$, and the organic layer was extracted with CH_2Cl_2. The organic phase was washed with water and brine, and dried over Na_2SO_4. After removal of the solvent, the mixture was purified by silica-gel column chromatography to give pure **12** as a white powder (1.61 g, 56% yield).

Preparation of 2,2′-bis(2,2,2-trifluoro-1-hydroxyethyl)-6-trifluoromethyldipyrromethane 13: *meso*-Trifluoromethyl-substituted dipyrromethane **10**

Table 1. Crystallographic details for **3**, **4**, **6**, **7**, and **14**.

	3	**4**	**6**	**7**	**14**
formula	$C_{30}N_5F_{15}H_{12}$	$C_{36}N_6F_{18}H_{16}$	$C_{61}N_{10}F_{30}H_{26}Cl_2$	$C_{80}N_{12}F_{36}H_{34}OCl_2$	$C_{36}N_6F_{18}H_{14}$
M_r	727.45	874.53	1539.80	1934.09	872.53
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2/c$ (13)	$P2_1/n$ (14)	$P2_1/c$ (14)
a [Å]	8.3513(8)	11.2767(8)	8.50(1)	12.0151(7)	8.4856(10)
b [Å]	10.9428(10)	11.3922(2)	12.06(2)	40.273(2)	41.522(5)
c [Å]	15.4333(14)	13.9713(8)	28.41(4)	16.0233(10)	9.8799(11)
α [°]	104.309(2)	108.486(4)	90	90	90
β [°]	97.035(2)	96.708(6)	95.7(1)	98.183(1)	103.642(2)
γ [°]	100.594(2)	96.264(8)	90	90	90
V [Å^3]	1322.3(2)	1670.1(2)	2898.5(8)	7674.4(8)	3382.9(7)
Z	2	2	2	4	4
ρ_{calcd} [g cm^{-3}]	1.827	1.739	1.764	1.674	1.713
$\mu(Mo_{K\alpha})$ [cm^{-1}]	1.85	1.76	2.63	2.30	1.74
$F(000)$	724	872	1532	3856	1736
crystal size [mm^3]	$0.45\times0.20\times0.02$	$0.30\times0.20\times0.15$	$0.25\times0.15\times0.05$	$0.20\times0.20\times0.10$	$0.40\times0.20\times0.10$
$2\theta_{max}$ [°]	56.6	54.7	55.0	50.0	56.4
total reflections	8592	14151	22208	40720	20302
unique reflections	5962	7269	6605	13505	7643
reflection used	5962	4821	2452	13505	7643
parameters	451	569	470	1140	597
absorption correction	empirical	–	–	empirical	empirical
R_1	0.0707	0.060	0.099	0.0823	0.0704
wR_2	0.1471	0.072	0.113	0.2201	0.1645
GOF	1.131	1.300	1.254	1.050	1.158

(2.14 g, 10 mmol) was dissolved in toluene (60 mL). Trifluoroacetic anhydride (6.9 mL, 50 mmol) was added to the solution at room temperature, and the resultant solution was stirred for 5 h. Then the reaction mixture was poured into aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic extracts were washed with water and brine, and dried over Na_2SO_4. After removal of the solvent, recrystallization in dichloromethane and hexane gave diacylated dipyrromethane as a white solid (3.56 g, 88% yield). Reduction with $NaBH_4$ in THF and MeOH gave **13** quantitatively as yellow oil.

[3+2]Condensation reaction of 12 and 13: Compounds **12** (120 mg, 0.33 mmol) and **13** (135 mg, 0.33 mmol) were dissolved in dichloromethane (5 mL, 66 mM). After the addition of methanesulfonic acid (10.7 μl, 0.5 equiv), the resultant solution was refluxed for 12 h and then was treated with DDQ (170 mg, 2.3 equiv) at room temperature for 6 h. The reaction mixture was neutralized by washing with aqueous $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent, the mixture was separated into each fractions to give **3**, **8**, and **9** in 1–2%, ~1.5%, and 4–5% yields, respectively.

***meso*-Trifluoromethyl-substituted [18]porphyrin 2**: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 9.62$ (s, 8H; β-CH), −2.08 ppm (s, 2H; NH); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): $\delta = -39.03$ ppm (s, 12F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 404 (126000), 510 (9900), 545 (9900), 594 (4800), 649 nm ($10000\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 581.0640 (100) $[M-H]^-$; calcd for $C_{24}N_4F_{12}H_9$: 581.0641.

***meso*-Trifluoromethyl-substituted [24]NFP$_5$ 3**: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): $\delta = 9.26$ (s, 1H; NH), 8.62 (s, 1H; NH), 8.05 (s, 1H; NH), 7.80 (dd, $J = 5.3$, 2.8 Hz, 1H; β-CH), 7.63–7.59 (m, 2H; β-CH), 7.52 (dd, $J = 5.0$, 2.3 Hz, 1H; β-CH), 7.28 (d, $J = 5.9$ Hz, 1H; β-CH), 7.12 (dd, $J = 7.0$, 2.3 Hz, 1H; β-CH), 6.43 (brs, 1H; β-CH), 5.95 (t, $J = 3.2$ Hz, 1H; β-CH), 3.09 ppm (d, $J = 1.4$ Hz, 1H; β-CH); ^{19}F NMR (565 MHz, CD_2Cl_2, 298 K): $\delta = -50.54$ (s, 3F), −51.06 (s, 3F), −56.58 (s, 3F), −56.65 (s, 3F), −57.56 ppm (s, 3F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 361 (23000), 472 (34900), 643 nm ($7500\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 726.0771 (100) $[M-H]^-$; calcd for $C_{30}N_5F_{15}H_{11}$: 726.0780.

***meso*-Trifluoromethyl-substituted [28]hexaphyrin 4**: ^{1}H NMR (600 MHz, CD_2Cl_2, 193 K): $\delta = 14.99$ (s, 2H; NH), 12.14 (s, 2H; NH), 7.43 (d, $J =$ 2.0 Hz, 2H; β-CH), 7.23 (s, 2H; β-CH), 7.00 (s, 2H; β-CH), 6.95 (s, 2H; β-CH), 6.90 (d, $J = 2.8$ Hz, 2H; β-CH), 6.77 ppm (s, 2H; β-CH); ^{19}F NMR (565 MHz, CD_2Cl_2, 193 K): $\delta = -55.40$ (s, 6F), −56.65 (s, 6F), −57.51 ppm (s, 6F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 312 (22600), 506 (62700), 557 nm ($66800\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 873.1064 (100) $[M-H]^-$; calcd for $C_{36}N_6F_{18}H_{15}$: 873.1076.

***meso*-Trifluoromethyl-substituted [32]heptaphyrin 5**: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 15.68$ (s, 2H; NH), 11.15 (s, 2H; NH), 9.93 (s, 2H; β-CH), 8.90 (s, 2H; β-CH), 7.79 (s, 2H; β-CH), 7.56 (s, 2H; β-CH), 6.60 ppm (m, 6H; β-CH); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): $\delta =$ −50.72 (s, 6F), −51.17 (s, 3F), −55.26 (s, 6F), −57.46 ppm (s, 6F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 363 (42000), 572 nm ($66500\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 1018.1213 (100) $[M-H]^-$; calcd for $C_{42}N_7F_{21}H_{17}$: 1018.1216.

***meso*-Trifluoromethyl-substituted [46]decaphyrin 6**

Conformer ***6-I***: ^{1}H NMR (600 MHz, $CDCl_3$, 213 K): $\delta = 8.32$ (brs, 1H; β-CH), 8.21 (dd, $J = 4.8$, 2.8 Hz, 1H; β-CH), 8.16 (s, 1H; NH), 7.94 (d, $J =$ 4.1 Hz, 1H; β-CH), 7.84 (d, $J = 2.1$ Hz, 1H; β-CH), 7.78 (m, 1H; β-CH), 7.76 (dd, $J = 4.8$, 2.0 Hz, 1H; β-CH), 7.67 (dd, $J = 2.0$, 2.0 Hz, 1H; β-CH), 7.60 (d, $J = 2.8$ Hz, 1H; β-CH), 7.57 (s, 1H; β-CH), 7.41 (brs, 1H; β-CH), 7.20–7.19 (m, 2H; β-CH), 7.14 (s, 1H; NH), 6.74 (brs, 1H; β-CH), 6.59 (d, $J = 5.5$ Hz, 1H; β-CH), 6.56 (d, $J = 3.5$ Hz, 1H; β-CH), 6.49 (dd, $J =$ 4.1, 2.0 Hz, 1H; β-CH), 6.37 (s, 1H; β-CH), 5.86 (d, $J = 4.8$ Hz, 1H; β-CH), 5.82 (s, 1H; NH), 4.83 (s, 1H; β-CH), 4.30 (s, 1H; β-CH), 3.44 (s, 1H; NH), 3.34 (s, 1H; NH), 1.08 ppm (s, 1H; NH); ^{19}F NMR (565 MHz, $CDCl_3$, 213 K): $\delta = -44.55$ (s, 6F), −46.02 (s, 3F), −47.04 (s, 3F), −47.84 (s, 3F), −48.44 (s, 3F), −49.39 (s, 3F), −54.87 (s, 3F), −56.64 (s, 3F), −58.53 ppm (s, 3F)

Conformer ***6-II***: ^{1}H NMR (600 MHz, $CDCl_3$, 213 K): $\delta = 12.45$ (s, 2H; NH), 10.72 (s, 2H; NH), 10.61 (s, 2H; NH), 7.73 (brs, 2H; β-CH), 7.60 (2H; a β-CH peak was hidden in the peak due to the conformer **6-I**), 7.48 (d, $J = 2.8$ Hz, 2H; β-CH), 7.34 (brs, 2H; β-CH), 7.31 (dd, $J = 5.4$, 2.1 Hz, 2H; β-CH), 7.26 (2H; a β-CH signal was hidden in the peak due to the residual $CHCl_3$), 7.16 (d, $J = 2.8$ Hz, 2H; β-CH), 7.13 (s, 2H; β-CH), 6.80 (brs, 2H; β-CH), 6.77 ppm (dd, $J = 4.8$, 2.8 Hz, 2H; β-CH); ^{19}F NMR (565 MHz, $CDCl_3$, 213 K): $\delta = -50.93$ (s, 6F), −51.97 (s, 6F), −52.18 (s, 6F), −54.54 (s, 6F), −59.18 ppm (s, 6F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 364 (51200), 447 (60800), 746 (50000) 1036 nm ($14600\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 1455.1784 (100) $[M-H]^-$; calcd for $C_{60}N_{10}F_{30}H_{25}$: 1455.1790.

***meso*-Trifluoromethyl-substituted [56]dodecaphyrin 7**

Conformer ***7-I***: ^{1}H NMR (600 MHz, CD_2Cl_2, 183 K): $\delta = 12.80$ (s, 2H; NH), 9.40 (s, 2H; NH), 8.92 (s, 2H; β-CH), 8.35 (s, 2H; β-CH), 8.23 (s, 2H; NH), 7.74 (s, 2H,; β-CH), 7.32 (s, 2H; β-CH), 7.13 (s, 2H; β-CH), 7.04–6.98 (m, 8H; β-CH), 6.78 (s, 2H; β-CH), 6.74 (s, 2H; β-CH), 6.46 (s, 2H; β-CH), 6.31 ppm (s, 2H; NH); ^{19}F NMR (565 MHz, CD_2Cl_2, 183 K); $\delta = -45.00$ (s, 6F), −49.34 (s, 6F), −51.18 (s, 6F), −54.78 (s, 6F), −56.33 (s, 6F), −59.47 ppm (s, 6F).

Conformer ***7-II***: ^{19}F NMR (565 MHz, CD_2Cl_2, 183 K); $\delta = -44.06$ (s, 3F), −45.88 (s, 3F), −49.50 (s, 3F), −50.20 (s, 3F), −51.37 (s, 3F), −53.39 (s, 3F), −53.82 (s, 3F), −56.59 (s, 3F), −56.75 (s, 3F), −56.99 (s, 3F), −57.33 (s, 3F), −57.61 ppm (s, 3F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 345 (52100), 397 (53600), 532 (73900), 778 nm ($57900\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 1747.2201 (100) $[M-H]^-$; calcd for $C_{72}N_{12}F_{36}H_{31}$: 1747.2225.

***meso*-Hydroxy-substituted calix[5]phyrin 8**: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 10.02$ (s, 2H; NH), 9.22 (s, 1H; NH), 7.84 (m, 4H; β-CH), 7.55 (d, $J = 4.1$ Hz, 2H; β-CH), 7.42 (d, $J = 4.6$ Hz, 2H; β-CH), 4.94 (d, $J = 1.9$ Hz, 2H; β-CH), 2.23 ppm (s, 1H; OH); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): $\delta = -53.65$ (m, 6F), −55.59 (s, 6F), −82.85 ppm (s, 3F); ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): $\delta = 151.3$, 146.1, 141.4, 139.5, 135.8, 131.5, 130.4, 129.2, 125.6, 124.7, 123.9, 123.7, 122.2, 115.6, 100.6, 73.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 358 (29400), 481 (55200), 673 nm ($8100\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 744.0855 (100) $[M-H]^-$; calcd for $C_{30}N_5F_{15}H_{13}O$: 744.0886.

***meso*-Trifluoromethyl-substituted calix[5]phyrin 9**: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 10.81$ (s, 2H; NH), 9.19 (s, 1H; NH), 7.74–7.73 (m, 4H; β-CH), 7.45 (d, $J = 4.1$ Hz, 2H; β-CH), 7.34 (d, $J = 4.1$ Hz, 2H; β-CH), 5.26 (d, $J = 1.9$ Hz, 2H; β-CH), 2.64 ppm (q, $J = 8.8$ Hz, 1H; CH); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): $\delta = -52.79$ (s, 6F), −54.59 (s, 6F), −70.16 ppm (d, $J = 8.7$ Hz, 3F); ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): $\delta =$ 151.8, 146.4, 140.3, 139.7, 136.4, 131.7, 130.1, 128.3, 125.0, 124.8, 123.9, 123.6, 122.9, 116.7, 100.8, 47.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 359 (34700), 466 (57200), 663 nm ($10100\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 728.0913 (100) $[M-H]^-$; calcd for $C_{30}N_5F_{15}H_{13}$: 728.0937.

***meso*-Trifluoromethyl-substituted [26]hexaphyrin 14**: MnO_2 (Chemicals Treated, 23 mg, 0.26 mmol) was added to a solution of compound **4** (10 mg, 11 μmol) in CH_2Cl_2 (15 mL). The resulting solution was stirred for 20 min to give an violet solution, which was filtered and evaporated to afford compound **14** quantitatively. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 11.11$ (s, 2H; NH), 7.88 (m, 2H; β-CH), 7.67 (m, 2H; β-CH), 7.54 (dd, $J = 4.6$, 2.0 Hz, 2H; β-CH), 7.38 (d, $J = 2.7$ Hz, 2H; β-CH), 6.33 (d, $J = 4.8$ Hz, 2H; β-CH), 5.99 ppm (dd, $J = 4.8$, 2.1 Hz, 2H; β-CH); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): $\delta = -51.73$ (s, 6F), −53.32 (s, 6F), −55.81 ppm (s, 6F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 329 (38100), 391 (20000), 581 (90300), 748 nm ($9700\,M^{-1}cm^{-1}$); HR-ESI-TOF-MS: *m/z* (%): 873.1061 (100) $[M+H]^+$; calcd for $C_{36}N_6F_{18}H_{15}$: 873.1065.

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[20] Increasing of the amount of MSA caused a drop in the yields of the expanded porphyrins. Uses of Brønsted and Lewis acids both assisted the formation of *meso*-trifluoromethyl-substituted expanded porphyrins, but the yields of the expanded porphyrins were clearly lower in the reactions with $BF_3{\cdot}OEt_2$ (0.1 equiv) and TFA (1.0 equiv).

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