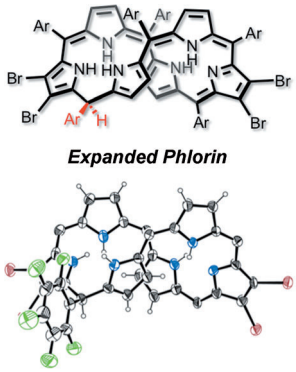
FULL PAPER

Exphlorin′ all avenues: 2,3,17,18-Tetrahalohexaphyrins were prepared by acid-catalyzed condensation of 3,4-dihalopyrroles and dipyrromethanedicarbinol. These β-tetrahalogenated hexaphyrins display variable structural and electronic properties depending upon the halogen atom and the number of π-electrons. Tetrabromo- and tetrachloro[28]hexaphyrin were further reduced to provide phlorin-type hexaphyrins.



Porphyrinoids

Tomohiro Higashino,
*Atsuhiro Osuka** ____ ▮▮▮▮–▮▮▮▮

2,3,17,18-Tetrahalohexaphyrins and the First Phlorin-type Hexaphyrins

DOI: 10.1002/asia.201300474

VIP

2,3,17,18-Tetrahalohexaphyrins and the First Phlorin-type Hexaphyrins

Tomohiro Higashino and Atsuhiro Osuka*[a]

Abstract: 1-(Triisopropylsilyl)-3,4-dichloropyrrole and 1-(triisopropylsilyl)-3,4-difluoropyrrole were conveniently prepared from the corresponding 3,4-dibromopyrrole by lithiation followed by halogenation. 2,3,17,18-Tetrahalogeno [26]- and [28]hexaphyrins have been prepared by condensation of 3,4-dihalopyrroles and a dipyrromethane-dicarbinol. 2,3,17,18-Tetrahalogenated hexaphyrins display variable structural and electronic properties depending upon the halogen atom and the number of π-electrons. Tetrabromo[28]hexaphyrin and tetrachloro[28]hexaphyrin were further reduced with excess $NaBH_4$ to furnish *meso*-reduced hexaphyrins as the first example of phlorin-type *meso*-aryl-substituted hexaphyrins.

Keywords: aromaticity · expanded porphyrins · halogenation · hexaphyrin · phlorin

Introduction

Expanded porphyrins have emerged as a novel class of porphyrinoids in light of their intriguing structural, chemical, and electronic properties.[1] Recently, we have found that modification to the periphery of expanded porphyrins is an effective strategy for tuning and controlling their structural and electronic properties.[2] To demonstrate this strategy, we report here the synthesis and characterizations of 2,3,17,18-tetrahalohexaphyrins. In the case of porphyrins, 2,3,12,13-tetrahalogenation leads to structural distortions, red-shifted absorption bands, and lowered electrochemical potentials, but these changes are relatively small.[3] By contrast, it would be expected that 2,3,17,18-tetrahalogenation of [26]hexaphyrin **1** and [28]hexaphyrin **2** would induce much larger perturbations since hexaphyrins are more flexible in terms of their electronics and structure.[4]

During the course of this study we found that tetrabromo- and tetrachloro[28]hexaphyrins are, upon treatment with excess $NaBH_4$, further reduced to furnish *meso*-hydro species. These *meso*-hydro species are the first example of phlorin-type hexaphyrins. Two-electron reduced porphyrins, such as chlorin (2,3-dihydroporphyrin), isophlorin (*N*,*N*′-dihydroporphyrin), and phlorin (5,22-dihydroporphyrin) (Figure 1), have attracted considerable attention because of their intriguing photophysical and redox properties. In particular, phlorins, which were first noted by Woodward in the 1960s,[5] possess non-cyclic conjugated electronic networks owing to a saturated sp^3 *meso*-carbon atom and show optical properties that are drastically altered from 18π-conjugated cyclic porphyrinoids. Studies of phlorins have also been motivated by anion-binding properties and intense Q-bands in the visible region.[6] However, the intrinsic instability of phlorins towards oxidation has hampered detailed studies.[7] In this context, stable phlorins that are chemically robust towards standard synthetic manipulations are highly desirable.[8–10] Similarly to cases of reduced porphyrins, a reduced class of expanded porphyrins also remains elusive. Recently, examples of chlorin-[11] and isophlorin-type[2e,12,13] expanded porphyrins have been reported. However, no phlorin-type expanded porphyrins have been reported thus far.

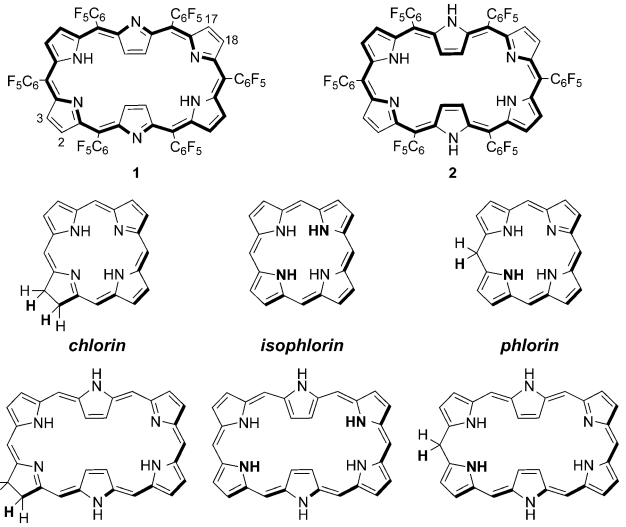


Figure 1. Reduced porphyrins and hexaphyrins.

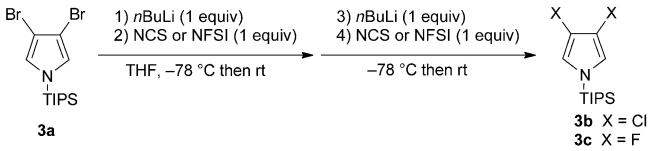
Results and Discussion

By following an existing protocol,[14] 3,4-dibromopyrrole **3a** was prepared by bromination of *N*-(triisopropylsilyl)pyrrole

[a] T. Higashino, Prof. Dr. A. Osuka
Department of Chemistry
Graduate School of Science
Kyoto University
Sakyo-ku, Kyoto, 606-8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp

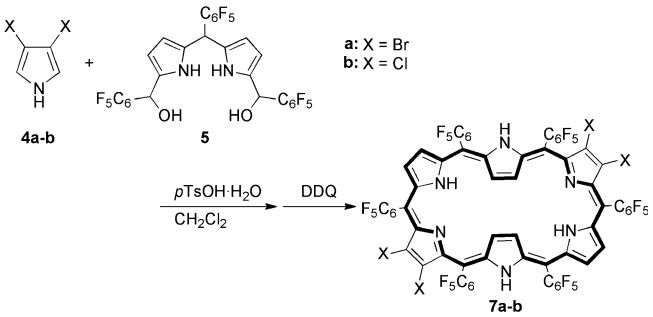
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201300474.

with *N*-bromosuccinimide (NBS) in THF in 84% yield. Previously, pyrrole **3a** was used to prepare various 3,4-disubstituted pyrroles by an initial treatment with *n*BuLi followed by the reaction with a suitable electrophile.[2e,14] Encouraged by these results, we attempted to prepare the corresponding 3,4-dichloro- and 3,4-difluoropyrroles, **3b** and **3c**, from **3a**. After extensive optimization of reaction conditions, we obtained **3b** in 50% yield by a complicated procedure. Firstly, one equivalent of *n*BuLi was added dropwise to a solution of **3a** in THF at −78°C. After stirring for 15 min, a solution containing one equivalent of *N*-chlorosuccinimide (NCS) in THF was added, with stirring continuing for a further 30 min at room temperature. The reaction was then cooled to −78°C followed by the addition of one more equivalent of *n*BuLi. Stirring was allowed to continue for a further 30 min, followed by the addition of one more equivalent of NCS. The reaction mixture was then allowed to warm to room temperature and left to stir for a further 30 min (Scheme 1). *N*-protected 3,4-difluoropyrrole **3c** was obtained in 42% yield by a similar procedure that utilized *N*-fluorobenzenesulfonimide (NFSI) as the electrophile. It is worth to emphasize that this protocol is scalable, as demonstrated by the preparation of **3c** (1.2 g) from **3a** (3.8 g) in 48% yield. As will be reported later, pyrrole **3c** is easily deprotected upon treatment with tetrabutylammonium fluoride (TBAF) to generate 3,4-difluoropyrrole, which is a valuable building block for electron-deficient porphyrinoids and calixarenes.[2a,15,16] This method of preparing 3,4-difluoropyrrole is much simpler and convenient in comparison to previous methods.[17]

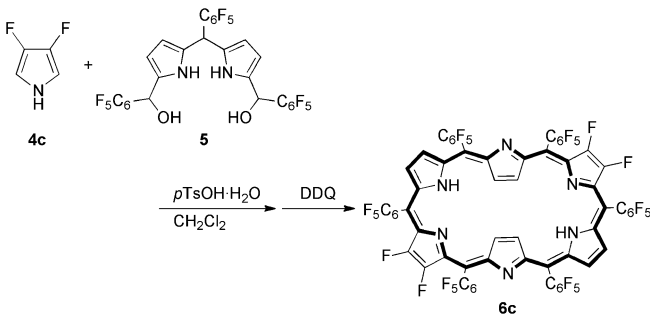


Scheme 1. Syntheses of 1-triisoprpylsilyl-3,4-dihalopyrroles **3b** and **3c**.

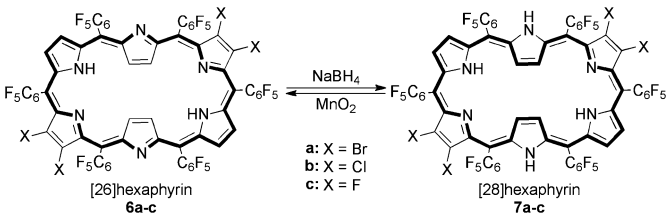
In the next step, we examined the synthesis of 2,3,17,18-tetrahalohexaphyrins according to Schemes 2 and 3. 3,4-Dihalopyrroles **4a–c** were generated by deprotection of **3a–c** with TBAF, and were used directly in an acid-catalyzed condensation reaction with dipyrromethane-dicarbinol **5**.[18] Condensation of **4a** with **5** followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded 2,3,17,18-tetrabromo[28]hexaphyrin **7a** in 3.7% yield (Scheme 2). The high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectrum of **7a** exhibits the parent ion peak at $m/z = 1778.7402$ (calcd for $C_{66}H_{13}Br_4F_{30}N_6$, $[M+H]^+$: 1778.7423), which is consistent with its 28π electronic state. Under similar conditions, the reaction of **4b** with **5** afforded 2,3,17,18-tetrachloro[28]hexaphyrin **7b** in 5.4% yield (Scheme 2). The HR-ESI-TOF mass spectrum of **7b** exhibits the parent ion peak at $m/z =$ 1600.9438 (calcd for $C_{66}H_{13}Cl_4F_{30}N_6$, $[M+H]^+$: 1600.9458), which also indicates its 28π electronic state. Differing from these results, the reaction of **4c** with **5** under similar conditions provided 2,3,17,18-tetrafluoro[26]hexaphyrin **6c** in 11% yield (Scheme 3). The HR-ESI-TOF mass spectrum of **6c** displays the parent ion peak at $m/z = 1533.0509$ (calcd for $C_{66}H_{11}F_{34}N_6$, $[M+H]^+$: 1533.0497), confirming its 26π electronic state. Since [28]hexaphyrins **7a** and **7b** were unexpectedly obtained in the reactions of **4a** and **4b** with **5**, we examined the redox interconversions of these hexaphyrins. As indicated in Scheme 4, [26]hexaphyrins **6a–c** and [28]hexaphyrins **7a–c** were quantitatively interconvertible through reduction with $NaBH_4$ and oxidation with MnO_2.



Scheme 2. Syntheses of 2,3,17,18-tetrahalo[28]hexaphyrin **7a**,**b**.



Scheme 3. Synthesis of 2,3,17,18-tetrafluoro[26]hexaphyrin **6c**.



Scheme 4. Redox interconversions of **6** and **7**.

Since the ^1H NMR spectra of [26]hexaphyrins **6a** and **6b** display similar temperature-dependent behaviors, only the spectrum of **6a** is discussed here in detail. The spectrum of **6a** exhibits broad resonances at 25°C, suggesting rapid conformational interconversion, but becomes sharper upon cooling to −60°C, displaying three distinct sets of peaks. One set consists of two peaks due to the β-protons at δ =

9.07 and 8.86 ppm and a peak due to the NH protons at $\delta =$ 0.81 ppm, and second set consists of two peaks due to the outer β-protons at $\delta = 9.18$ and 8.83 ppm, two peaks due to the inner β-protons at $\delta = -0.17$ and -0.50 ppm, and a resonance due to the inner NH protons at $\delta = -0.35$ ppm. These spectral features allow us to assign these sets as conformers A and B (Figures 2 and 3a). The third set consists of a resonance due to the NH protons at $\delta = 8.64$ ppm and four peaks due to the β-protons at $\delta = 7.37$, 7.13, 5.73, and 4.73 ppm, which have been assigned to the figure-of-eight conformer C. The ratio of A:B:C has been determined to be 15:50:35, indicating that conformer B predominates in solution. The ^{1}H NMR spectrum of **6b** in $CDCl_3$ at -60 °C also exhibits three similar sets of peaks assignable to conformers A, B, and C with a ratio of 4:80:16, thereby indicating again that conformer B predominates in solution (see the Supporting Information). By contrast, the ^{1}H NMR spectrum of **6c** is relatively straightforward, showing that a single conformer A resides in solution. The rectangular structure of **6a** (conformer A) has been supported by preliminary X-ray structural analysis (see the Supporting Information). We assume that the appended β-halogen atom exerts a steric influence that is crucial in determining the conformational distribution.

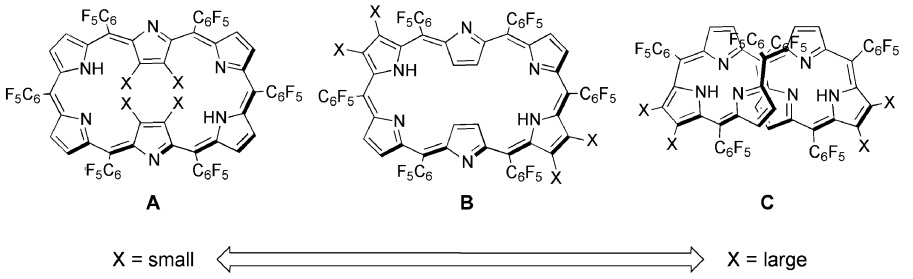


Figure 2. Three conformers A, B, and C of [26]hexaphyrins in solution.

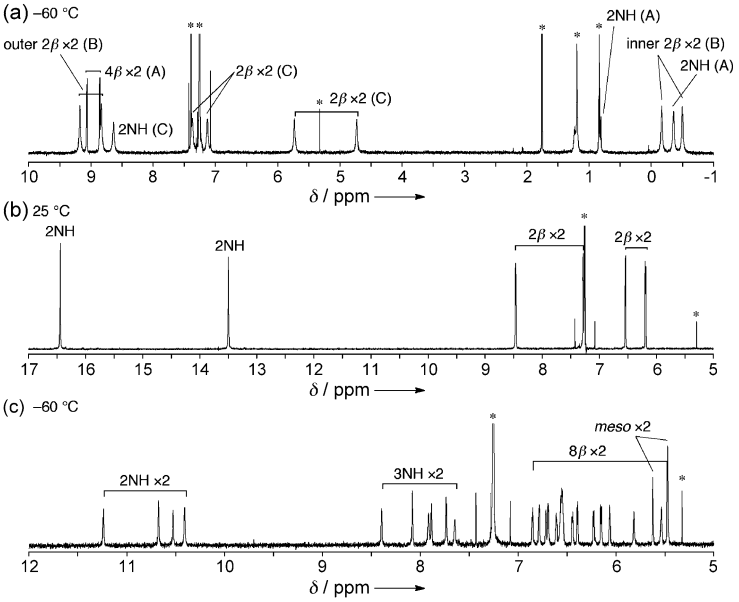


Figure 3. ^{1}H NMR spectra of (a) **6a**, (b) **7a**, and (c) **8a** in $CDCl_3$. Peaks marked with an asterisk are due to residual solvents. In panel a, assignments of peaks are also indicated.

The structure of **7a** has been determined by X-ray diffraction analysis to be a figure-of-eight conformation (Figure 4a).[19a] The four bromine atoms are located at the least hindered β-positions on the periphery. The ^{1}H NMR spectrum of **7a** shows two peaks due to the NH protons at $\delta =$ 16.43 and 13.49 ppm, and four peaks due to the β-protons at $\delta = 8.46$, 7.28, 6.54, and 6.19 ppm (Figure 3b). These data indicate that **7a** adopts a single figure-of-eight conformation in solution. The ^{1}H NMR spectrum of **7b** is very similar to that of **7a**, displaying similar resonances; two peaks due to the NH protons at $\delta = 16.55$ and 13.37 ppm, and four peaks due to the β-protons at $\delta = 8.39$, 7.20, 6.56, and 6.18 ppm. These data indicate that **7b** also adopts a single figure-of-eight conformation. On the other hand, the ^{1}H NMR spectrum of **7c** is broad at 25 °C, reflecting its dynamic conformational equilibrium in solution similar to non-halogenated [28]hexaphyrin **2**.[4] At -40 °C the spectrum becomes less broad, showing a spectral pattern similar to the spectrum of **2** at room temperature. These results were interpreted in terms of conformational dynamics involving Möbius aromatic conformers and the Hückel aromatic conformer (Figure 5).

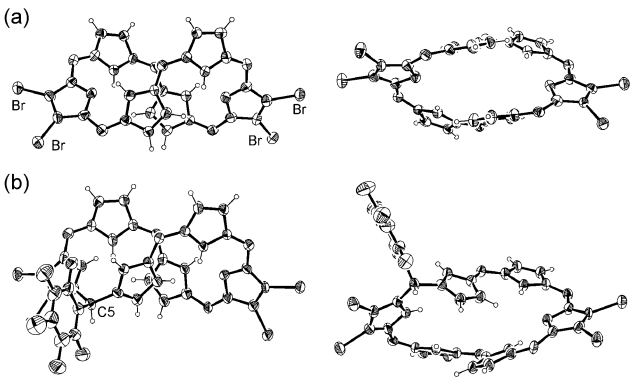


Figure 4. X-ray crystal structures of (a) **7a** and (b) **8a**. Top view (left) and side view (right). Thermal ellipsoids represent 30% probability. Solvent molecules and *meso*-aryl substituents are omitted for clarity except for the sp^3-*meso* position.

Figure 6a,b displays the UV/Vis absorption spectra of [26]hexaphyrins **6a–c** and [28]hexaphyrins **7a–c** in CH_2Cl_2, respectively. All [26]hexaphyrins show Soret-like bands and Q-like bands, indicating their 26π aromatic character. The wavelengths of Soret- and Q-like bands of [26]hexaphyrins are summarized in Table 1. [26]Hexaphyrin **6c** shows almost no shift compared with the parent [26]hexaphyrin **1**, while both Soret- and Q-like bands of [26]hexaphyrins **6a** and **6b**

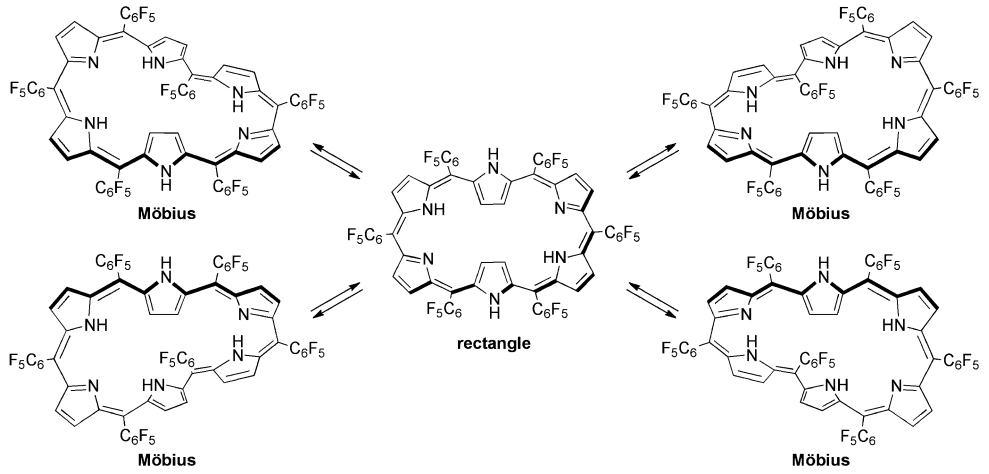


Figure 5. Dynamic conformational equilibrium of **2** in solution.

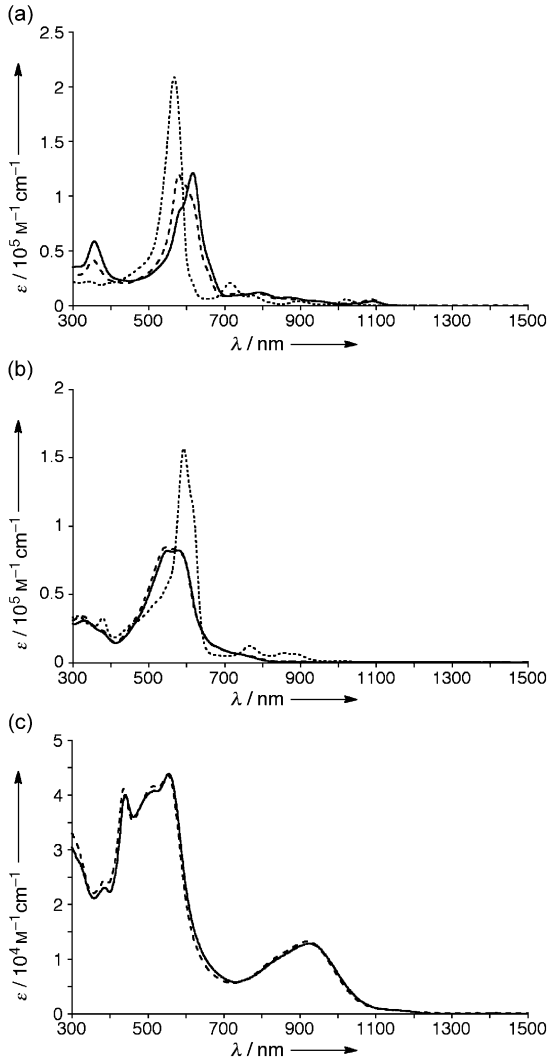


Figure 6. UV/Vis absorption spectra of (a) **6a–c**, (b) **7a–c**, and (c) **8a**,**b** in CH_2Cl_2: **6–8a** (——), **6–8b** (– – –), and **6–7c** (•••••).

are red-shifted by 10–70 nm, which are similar to values observed for β-halogentated porphyrins.[3a,c] On the other hand, [28]hexaphyrins **7a** and **7b** display ill-defined Soret-like bands at 550–580 nm and almost no Q-like bands, which is consistent with weak 28π antiaromaticity and a figure-of-eight conformation. By contrast, [28]hexaphyrin **7c** exhibits an intense Soret-like band at 593 nm and Q-like bands at 766, 854, 885, and 1013 nm, indicating significant contribution of 28π Möbius aromatic conformers. This assignment is consistent with the ^{1}H NMR spectrum of **7c**. The electrochemical properties of halogenated [26]hexaphyrins **6a–c** and [28]hexaphyrins **7a–c** were studied by cyclic voltammetry in CH_2Cl_2 versus Fc/Fc^+ with tetrabutylammonium hexafluorophosphate as an electrolyte (Table 2). As expected, [26]hexaphyrins **6a–c** show lower first reduction potentials (−0.44 V for **6a**, −0.39 V for **6b**, and −0.39 V for **6c**) than **1** (−0.55 V), reflecting the electron-withdrawing effect of β-halogen atoms. Similarly, [28]hexaphyrins **7a–c** also display lower reduction and oxidation potentials (Table 2).

Finally, we examined the further reduction of [28]hexaphyrins **7a–c**. In analogy to [28]hexaphyrin **2**, **7c** was completely recovered upon treatment with a large excess of

Table 1. Selected optical properties of [26]hexaphyrins **6a–c** in CH_2Cl_2.

Hexaphyrin	Soret-like band, λ [nm]	Q-like band, λ [nm]
6a	592(sh), 616	790, 873, 945, 1090
6b	578, 592(sh)	729, 786, 1087
6c	567	714, 773, 894, 1021
1[a]	567	712, 769, 905, 1022

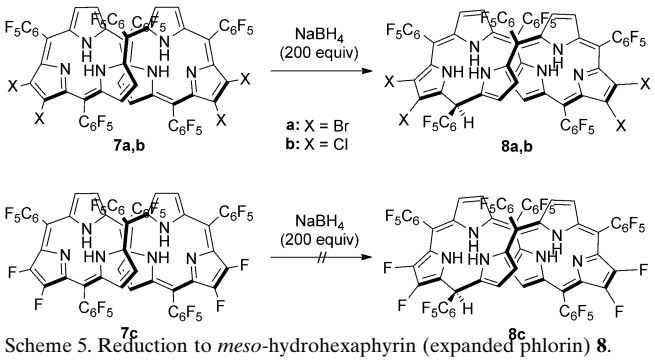
[a] Ref. [4].

Table 2. Electrochemical oxidation and reduction potentials $E_{1/2}$ vs Fc/Fc^+ in V for [26]hexaphyrins **6a–c** and **1**, and [28]hexaphyrins **7a–c** and **2**.

Hexaphyrins	E^{ox2}	E^{ox1}	E^{red1}	E^{red2}
6a	0.92[a]	0.83[a]	−0.44	−0.75
6b	–	0.95[a]	−0.39	−0.76
6c	1.05[a]	0.98[a]	−0.39	−0.74
1	–	0.86	−0.55	−0.88
7a	0.39	0.20	−0.76	−1.15
7b	0.36	0.19	−0.78	−1.16
7c	0.29	0.16	−0.88	−1.12
2	0.17	0.03	−1.11[a]	−1.50[a]

[a] Irreversible processes (E_p).

$NaBH_4$. By contrast, reaction of **7a** and **7b** with about 200 equivalents of $NaBH_4$ caused full conversion of the starting material, as assessed by thin-layer chromatography (TLC) analysis. After the usual aqueous work-up, separation by silica gel chromatography provided *meso*-hydro hexaphyrins **8a** and **8b** in 42 and 45% yield, respectively (Scheme 5). The structure of **8a** was revealed by X-ray diffraction analysis to be a figure-of-eight conformation with an sp^3-hybridized *meso*-carbon at the 5-position (Figure 4b).[19b] These findings indicate that **8a** is the first example of a phlorin-type hexaphyrin. The absorption spectrum of **8a** has an intense and broad Q-band at 923 nm, which is a characteristic signature of phlorin-type porphyrinoids[6b,7] (Figure 6c). The ^1H NMR spectrum of **8a** is rather broad at room temperature, suggesting rapid conformational interconversion, but becomes sharper at −60 °C, exhibiting two sets of signals (Figure 3c). Since hexaphyrin **8a** has one asymmetric *meso*-carbon (5-position) and a figure-of-eight structure, it is intrinsically chiral (*P*-twist or *M*-twist). The two sets of peaks have been assigned to equilibrating diastereomers (Figure 7). Reaction of **7a** with $NaBD_4$ produced *meso*-deuterated **8a** ([D]-**8a**). Two resonances corresponding to the *meso*-protons disappeared in the ^1H NMR spectrum of [D]-**8a** at −60 °C, thus indicating that $NaBH_4$ is the source of the hydrogen located at the 5-position (see the Supporting Information). Phlorin-type hexaphyrin **8b** also displays similar UV/Vis absorption and ^1H NMR spectra to that of **8a**. Phlorin-type hexaphyrins **8a** and **8b** are slightly sensitive to air but can be stored under nitrogen at −20 °C for about one month.



Scheme 5. Reduction to *meso*-hydrohexaphyrin (expanded phlorin) **8**.

Figure 7. Two diastereomers of **8a** observed in ^1H NMR at low temperature.

Conclusions

N-Protected 3,4-dichloropyrrole **3b** and 3,4-difluoropyrrole **3c** were conveniently prepared from *N*-protected 3,4-dibromopyrrole **3a**. 3,4-Dihalogenopyrroles were condensed with dipyrromethane dicarbinol **5** to produce 2,3,17,18-tetrahalo[26]hexaphyrins **6a–c** and [28]hexaphyrins **7a–c**. These 2,3,17,18-tetrahalogenated hexaphyrins display variable structural and electronic properties depending upon the β-substituted halogen atom and the number of π-electrons. [28]Hexaphyrins were further reduced with a large excess $NaBH_4$ to provide *meso*-hydro-hexaphyrins **8a** and **8b**, which are the first examples of phlorin-type hexaphyrins in the literature.

Experimental Section

General

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. *N*-bromosuccinimide (NBS) was recrystallized from benzene. Dry CH_2Cl_2 was obtained by refluxing and distillation over CaH_2. Silica-gel column chromatography was performed on Wakogel C-300 and C-400. Neutral alumina column chromatography was performed on Merck Aluminum oxide 90 active neutral. Alumina column chromatography was performed on Sumitomo Active alumina. UV/Vis absorption spectra were recorded with a Shimadzu UV-3600 spectrometer. ^1H and ^{19}F NMR spectra were recorded with a JEOL ECA-600 spectrometer (operating at 600.17 MHz for ^1H, 150.91 MHz for ^{13}C and 564.73 MHz for ^{19}F) by using the residual solvent as the internal reference for ^1H ($CDCl_3$: $\delta = 7.26$ ppm), the residual solvent as the internal reference for ^{13}C ($CDCl_3$: $\delta = 77.16$ ppm) and hexafluorobenzene as the external reference for ^{19}F ($\delta = -162.9$ ppm). NMR signals were assigned from the comparison with the spectra in the presence of D_2O (signals assigned for NH protons disappear in the presence of D_2O). Mass spectra were recorded with a BRUKER microTOF LC instrument by using the ESI-TOF method in the positive and negative ion mode in an acetonitrile solution. Single-crystal X-ray diffraction analysis data for compound **7a** and **8a** were collected at −180 °C with a Rigaku R-AXIS RAPID II diffractometer by using graphite monochromated Cu-K_a radiation ($\lambda = 1.54187$ Å). The structures were solved by using the direct method (SHELXS-97). Redox potentials were measured by cyclic voltammetry on an ALS electrochemical analyzer model 660. Hexaphyrins **1** and **2**,[20] *N*-(triisopropylsilyl)pyrrole,[14] and 1,10-bis(pentafluorobenzoyl)-5-pentafluorophenyl-dipyrromethane[18] were prepared as described.

*3,4-Dibromo-1-(triisopropylsilyl)pyrrole (**3a**)[14]*

A suspension of NBS (3.74 g, 21 mmol) in anhydrous THF (26 mL), which had been prepared at 0 °C, was added to a solution of *N*-(triisopropylsilyl)pyrrole (2.23 g, 10 mmol) in anhydrous THF (4 mL) at −78 °C and stirred for 30 min. Subsequently, the reaction mixture was slowly warmed to room temperature. Then *n*-hexane was added to the reaction mixture to precipitate the succinimide by-product, and the slurry was passed through a short neutral alumina column using *n*-hexane as eluent. After removal of the solvent, the residue was passed through a short silica gel column using *n*-hexane as eluent. The product was recrystallized from pentane at 0 °C to give **3a** as colorless solid (3.30 g, 84%). ^1H NMR (600.17 MHz, $CDCl_3$, 25 °C): $\delta = 6.72$ (s, 2H, α-H), 1.40 (septet, $J =$

7.4 Hz, 3H, -Si*CH*$(CH_3)_2$), and 1.09 ppm (d, J=7.4 Hz, 18H, -SiCH-(CH_3)$_2$).

*3,4-Dichloro-1-(triisopropylsilyl)pyrrole (**3b**)*

A solution of *n*BuLi in *n*-hexane (1.56 M, 0.64 mL, 1 mmol) was added to a solution of dibromopyrrole **3a** (381 mg, 1 mmol) in anhydrous THF (10 mL) at −78 °C under N_2 atmosphere and stirred for 15 min. Subsequently, a solution of NCS (133 mg, 1 mmol) in anhydrous THF (4 mL) was added, and the mixture was warmed to room temperature. The mixture was stirred for 30 min, then cooled to −78 °C again. Once more, a solution of *n*BuLi in *n*-hexane (1.56 M, 0.64 mL, 1 mmol) was added to the mixture and stirred for 30 min, followed by addition of a solution of NCS (133 mg, 1 mmol) in anhydrous THF (4 mL). The reaction mixture was warmed to room temperature and then stirred for 30 min. Next, the reaction was quenched with saturated NH_4Cl aqueous solution, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by silica gel chromatography using *n*-hexane to give **3b** as a colorless solid (145 mg, 50 %). ^{1}H NMR (600.17 MHz, $CDCl_3$, 25 °C): δ=6.66 (s, 2H, α-H), 1.40 (septet, J=7.4 Hz, 3H, -Si*CH*$(CH_3)_2$), and 1.09 ppm (d, J=7.4 Hz, 18H, -SiCH-(CH_3)$_2$); ^{13}C NMR (150.91 MHz, $CDCl_3$, 25 °C): δ=120.9, 113.0, 17.7, and 11.5 ppm; HRMS (ESI-TOF, positive) calcd. for $C_{13}H_{24}NCl_2Si$: 292.1050 $[M+H]^+$; found 292.1051.

*3,4-Difluoro-1-(triisopropylsilyl)pyrrole (**3c**)*

A solution of *n*BuLi in *n*-hexane (1.56 M, 6.4 mL, 10 mmol) was added to a solution of dibromopyrrole **3a** (3.81 g, 10 mmol) in anhydrous THF (100 mL) at −78 °C in N_2 atmosphere and stirred for 15 min. Subsequently, a solution of NFSI (3.15 g, 10 mmol) in anhydrous THF (20 mL) was added and the mixture was warmed to room temperature. The mixture was stirred for 1 h, then cooled to −78 °C again. Once more, a solution of *n*BuLi in *n*-hexane (1.56 M , 6.4 mL, 10 mmol) was added to the mixture and stirred for 30 min. Next, a solution of NFSI (3.15 g, 10 mmol) in anhydrous THF (20 mL) was added. The reaction mixture was warmed to room temperature and then stirred for 1 h. The reaction was quenched with saturated NH_4Cl aqueous solution, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After removal of the solvent, the crude product was passed through a short silica gel column using CH_2Cl_2 as eluent. The residue was purified by silica gel chromatography using *n*-hexane to give **3c** as pale yellow solid (1.24 g, 48 %). ^{1}H NMR (600.17 MHz, $CDCl_3$, 25 °C): δ=6.33 (s, 2H, α-H), 1.38 (septet, J=7.4 Hz, 3H, -Si*CH*$(CH_3)_2$), and 1.08 ppm (d, J=7.4 Hz, 18H, -SiCH-(CH_3)$_2$); ^{13}C NMR (150.91 MHz, $CDCl_3$, 25 °C): δ=140.7 (dd, J=240 Hz, J=13 Hz), 105.4 (dd, J=20 Hz, J=2.9 Hz), 17.7, and 11.5 ppm; ^{19}F NMR (564.73 MHz, $CDCl_3$, 25 °C): δ=−177.62 ppm (s, 2F); HRMS (ESI-TOF, positive) calcd. for $C_{13}H_{24}NF_2Si$: 260.1641 $[M+H]^+$; found 260.1639.

*Reduction to Dipyrromethane dicarbinol (**5**)*

1,10-Bis(pentafluorobenzoyl)-5-pentafluorophenyldipyrromethane (350 mg, 0.5 mmol) was reduced with $NaBH_4$ (379 mg, 10 mmol) in THF/MeOH (16.5 mL, 10:1). After stirring for 30 min, the reaction was quenched by addition of saturated NH_4Cl aqueous solution, and the product was extracted with EtOAc. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. The solvent was removed to yield dicarbinol **5** quantitatively; as it was unstable under ambient conditions, it had to be used instantly.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-2,3,17,18-tetrabromo[28]hexaphyrin(1.1.1.1.1.1) (**7a**)*

A solution of *n*Bu_4NF in THF (1.0 M, 0.55 mL, 0.55 mmol) was added to a solution of **3a** (190 mg, 0.5 mmol) in dry THF (10 mL) and stirred for 10 min. Next, the solvent was removed and the residue was passed through a short Florisil column using CH_2Cl_2 as eluent (50 mL). The resulting solution containing 3,4-dibromopyrrole **4a** was added to the solution of dicarbinol **5** (0.5 mmol) in dry CH_2Cl_2 (50 mL). *p*-Toluenesulfonic acid monohydrate (48 mg, 0.25 mmol) was added, and the mixture was stirred for 30 min under N_2 atmosphere in the dark at 0 °C. After adding 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 340 mg, 1.5 mmol), the resulting mixture was stirred for 2 h. The reaction mixture was directly passed through a short alumina column using CH_2Cl_2 as eluent, followed by evaporation of the solvent. Subsequent purification by silica gel column chromatography (CH_2Cl_2/*n*-hexane 1:4) provided **7a** as a violet fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave green crystals of **7a** (16.6 mg, 3.7 %). Single crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of 2-propanol into a solution of **7a** in 1,2-dichloroethane. ^{1}H NMR (600.17 MHz, $CDCl_3$, 25 °C): δ=16.43 (brs, 2H, NH), 13.49 (brs, 2H, NH), 8.46 (brs, 2H, β-H), 7.28 (brs, 2H, β-H), 6.54 (d, J=4.8 Hz, 2H, β-H), and 6.19 ppm (d, J=4.8 Hz, 2H, β-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, 25 °C): δ=−136.48 (d, J=17.3 Hz, 2F, *ortho*-F), −137.33 (d, J=20.7 Hz, 2F, *ortho*-F), −137.69 (m, 2F, *ortho*-F), −139.04 (d, J=17.3 Hz, 2F, *ortho*-F), −139.56 (m, 2F, *ortho*-F), −140.18 (m, 2F, *ortho*-F), −149.84 (t, J=20.7 Hz, 2F, *para*-F), −151.26 (t, J=20.7 Hz, 2F, *para*-F), −152.94 (t, J=20.7 Hz, 2F, *para*-F), −158.54 (t, J=20.7 Hz, 2F, *meta*-F), −159.63 (td, J=20.7 Hz, J=6.9 Hz, 2F, *meta*-F), −160.92 (brs, 2F, *meta*-F), −161.01 (m, 2F, *meta*-F), −161.38 (td, J=17.3 Hz, J=6.9 Hz, 2F, *meta*-F), and −161.69 ppm (td, J=20.7 Hz, J=6.9 Hz, 2F, *meta*-F); UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=330 (31000), 370(sh) (24000), 550 (82000), 578 (82000), 749(sh) (5800), and 871 (830) nm; HRMS (ESI-TOF, positive) calcd. for $C_{66}H_{13}Br_4F_{30}N_6$: 1778.7423 $[M+H]^+$; found 1778.7402.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-2,3,17,18-tetrabromo[26]hexaphyrin(1.1.1.1.1.1) (**6a**)*

MnO_2 (8.7 mg) was added to a solution of **7a** (8.9 mg, 5 μmol) in CH_2Cl_2 (10 mL), and the resulting solution was stirred for 1 h. The mixture was passed through a Celite pad and the solvent was removed. The crude product was purified by column chromatography using CH_2Cl_2 to give **6a** as a blue fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave violet crystals of **6a** quantitatively. ^{1}H NMR (600.17 MHz, $CDCl_3$, −60 °C) (conformer A): δ=9.07 (d, J=4.8 Hz, 4H, β-H), 8.86 (d, J=4.8 Hz, 4H, β-H) and 0.81 ppm (s, 2H, NH); (conformer B): δ=9.18 (brs, 2H, outer β-H), 8.83 (brs, 2H, outer β-H), −0.17 (brs, 2H, inner β-H), −0.35 (brs, 2H, NH) and −0.50 ppm (brs, 2H, inner β-H); (conformer C): δ=8.64 (brs, 2H, NH), 7.37 (brs, 2H, β-H), 7.13 (brs, 2H, β-H), 5.73 (brs, 2H, β-H), and 4.73 ppm (brs, 2H, inner β-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, 50 °C) (rectangle): δ=−137.13 (d, J=20.7 Hz, 4F, *ortho*-F), −138.07 (br, 8F, *ortho*-F), −150.11 (t, J=20.7 Hz, 2F, *para*-F), −150.37 (br, 2F, *para*-F), −153.78 (br, 2F, *para*-F), −160.52 (t, J=20.7 Hz, 4F, *meta*-F), −160.64 (br, 4F, *meta*-F), and −163.69 ppm (br, 4F, *meta*-F); UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=357 (60000), 592(sh) (91000), 616 (120000), 790 (12000), 873 (7600), 945 (4300) and 1090 nm (4000); HRMS (ESI-TOF, positive) calcd. for $C_{66}H_{11}Br_4F_{30}N_6$: 1776.7266 $[M+H]^+$; found 1776.7262.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-2,3,17,18-tetrachloro[28]hexaphyrin(1.1.1.1.1.1) (**7b**)*

A solution of *n*Bu_4NF in THF (1.0 M, 0.55 mL, 0.55 mmol) was added to a solution of **3b** (145 mg, 0.50 mmol) in dry CH_2Cl_2 (50 mL). After 5 min, the mixture was directly passed through a short Florisil column using CH_2Cl_2 as eluent (40 mL). The resulting solution containing 3,4-dichloropyrrole **4b** was added to the solution of dicarbinol **5** (0.50 mmol) in dry CH_2Cl_2 (10 mL). *p*-Toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) was added, and the mixture was stirred for 1 h under N_2 atmosphere in the dark at 0 °C. After addition of DDQ (227 mg, 1.0 mmol), the resulting mixture was stirred for 3 h. The reaction mixture was directly passed through a short alumina column using CH_2Cl_2 as eluent, followed by evaporation of the solvent. Subsequent purification by silica gel column chromatography (CH_2Cl_2/*n*-hexane 1:4) provided **7b** as a violet fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave green crystals of **7b** (21.6 mg, 5.4 %). ^{1}H NMR (600.17 MHz, $CDCl_3$, 25 °C): δ=16.55 (brs, 2H, NH), 13.37 (brs, 2H, NH), 8.39 (brs, 2H, β-H), 7.20 (brs, 2H, β-H), 6.56 (d, J=4.8 Hz, 2H, β-H), and 6.18 ppm (d, J=4.8 Hz, 2H, β-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, 25 °C): δ=−136.55 (brs, 2F, *ortho*-F), −137.29 (d, J=20.7 Hz, 2F, *ortho*-F), −137.63 (brs, 2F, *ortho*-F), −139.07 (d, J=17.3 Hz, 2F, *ortho*-F), −139.63 (d, J=17.3 Hz, 2F, *ortho*-F),

−140.35 (d, J=20.7 Hz, 2F, *ortho*-F), −149.79 (t, J=20.7 Hz, 2F, *para*-F), −151.17 (t, J=20.7 Hz, 2F, *para*-F), −152.90 (t, J=20.7 Hz, 2F, *para*-F), −158.53 (brs, 2F, *meta*-F), −159.66 (td, J=20.7 Hz, J=6.9 Hz, 2F, *meta*-F), −160.88 (m, 4F, *meta*-F), −161.28 (t, J=17.3 Hz, 2F, *meta*-F), and −161.63 ppm (t, J=20.7 Hz, 2F, *meta*-F). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=326 (34000), 375(sh) (24000), 545 (84000), 568 (83000), 743(sh) (6100) and 899 (1200) nm; HRMS (ESI-TOF, positive) calcd. for $C_{66}H_{13}Cl_4F_{30}N_6$:1600.9458 $[M+H]^+$; found 1600.9438.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-2,3,17,18-tetrachloro[26]hexaphyrin(1.1.1.1.1.1) (**6b**)*

MnO_2 (8.7 mg) was added to a solution of **7b** (8.0 mg, 5 μmol) in CH_2Cl_2 (10 mL), and the resulting solution was stirred for 1 h. The mixture was passed through a Celite pad and the solvent was removed. The crude product was purified by column chromatography using CH_2Cl_2 to give **6b** as a blue fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave violet crystals of **6b** quantitatively. ^{1}H NMR (600.17 MHz, $CDCl_3$, −60 °C) (conformer A): δ=9.17 (d, J=4.8 Hz, 4H, β-H), 8.96 (d, J=4.8 Hz, 4H, β-H) and 0.23 ppm (s, 2H, NH); (conformer B): δ=9.26 (d, J=3.5 Hz, 2H, outer β-H), 8.89 (d, J=3.5 Hz, 2H, outer β-H), −0.39 (s, 2H, inner β-H), −0.69 (s, 2H, NH) and −0.72 (s, 2H, inner β-H) ppm; (conformer C): δ=8.42 (brs, 2H, NH), 7.41 (brs, 2H, β-H), 7.17 (brs, 2H, β-H), 5.69 (brs, 2H, β-H) and 4.68 ppm (brs, 2H, β-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, −60 °C) (conformer A): δ=−136.06 (m, 4F, *ortho*-F), −136.38 (d, J=20.7 Hz, 4F, *ortho*-F), −137.28 (m, 4F, *ortho*-F), −148.48 (m, 2F, *para*-F), −149.61 (m, 4F, *para*-F), −159.50 (m, 4F, *meta*-F), −161.19 (m, 4F, *meta*-F), and −162.13 ppm (m, 4F, *meta*-F); UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=353 (40000), 578 (120000), 592(sh) (110000), 729 (11000), 786 (11000), and 1087 nm (6500); HRMS (ESI-TOF, positive) calcd. for $C_{66}H_{11}Cl_4F_{30}N_6$: 1598.9301 $[M+H]^+$; found 1598.9313.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-2,3,17,18-tetrafluoro[26]hexaphyrin(1.1.1.1.1.1) (**6c**)*

A solution of nBu$_4$NF in THF (1.0 M, 0.42 mL, 0.42 mmol) was added to a solution of **3c** (100 mg, 0.38 mmol) in dry CH_2Cl_2 (38 mL). After 5 min, the mixture was directly passed through a short Florisil column using CH_2Cl_2 as eluent (20 mL). The resulting solution containing 3,4-difluoropyrrole **4c** was added to the solution of dicarbinol **5** (0.38 mmol) in dry CH_2Cl_2 (10 mL). *p*-Toluenesulfonic acid monohydrate (36 mg, 0.19 mmol) was added, and the mixture was stirred for 1 h under N_2 atmosphere in the dark at 0 °C. After addition of DDQ (259 mg, 1.14 mmol), the resulting mixture was stirred for 3 h. The reaction mixture was directly passed through a short alumina column using CH_2Cl_2 as eluent, followed by evaporation of the solvent. Subsequent purification by silica gel column chromatography (CH_2Cl_2/*n*-hexane 3:2) provided **6c** as a violet fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave green crystals of **6c** (32 mg, 11 %). Single crystals for preliminary X-ray crystallographic analysis were obtained by vapor diffusion of methanol into solution of **6c** in 1,2-dichloroethane. ^{1}H NMR (600.17 MHz, $CDCl_3$, 25 °C): δ=9.36 (d, J=4.8 Hz, 4H, β-H), 9.09 (d, J=4.8 Hz, 4H, β-H), and −1.45 ppm (s, 2H, NH); ^{19}F NMR (564.73 MHz, $CDCl_3$, 25 °C): δ=−136.09 (dd, J=20.7 Hz, J=6.9 Hz, 4F, *ortho*-F), −136.85 (d, J=17.3 Hz, 8F, *ortho*-F), −145.82 (s, 4F, b-F), −149.34 (t, J=20.7 Hz, 2F, *para*-F), −152.01 (t, J=17.3 Hz, 4F, *para*-F), −159.97 (td, J=20.7 Hz, J=6.9 Hz, 4F, *meta*-F), and −162.48 ppm (t, J=17.3 Hz, 8F, *meta*-F). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=345 (23000), 567 (200000), 714 (21000), 773 (9900), 894 (5200), and 1021 nm (6600); HRMS (ESI-TOF, positive) calcd. for $C_{66}H_{11}F_{34}N_6$: 1533.0497 $[M+H]^+$; found 1533.0509.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-2,3,17,18-tetrafluoro[28]hexaphyrin(1.1.1.1.1.1) (**7c**)*

$NaBH_4$ (4 mg, 0.1 mmol) was added to a solution of **6c** (7.7 mg, 5 μmol) in CH_2Cl_2/MeOH (10 mL, 10:1), and the resulting solution was stirred at room temperature for 30 min under N_2 atmosphere. The reaction was quenched by addition of water, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. The crude product was purified by column chromatography using (CH_2Cl_2/*n*-hexane 1:1) to give **7c** as a blue fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave violet crystals of **7c** quantitatively. ^{1}H NMR (600.17 MHz, $CDCl_3$, 50 °C, Figure-of-eight): δ= 10.75 (brs, 2H, NH), 10.47 (brs, 2H, NH), 7.04 (brs, 2H, β-H), 6.91 (brs, 2H, β-H), 5.31 (brs, 2H, β-H), and 4.93 ppm (brs, 2H, β-H); ($CDCl_3$, −40 °C, rectangle): δ=8.63 (brs, 2H, outer-NH), 7.66 (brs, 2H, outer β-H), 7.50 (brs, 2H, outer β-H), 5.33 (brs, 2H, inner-NH), 2.91 (brs, 2H, inner β-H), and 2.32 ppm (brs, 2H, inner β-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, 25 °C): δ=−137.24 (brs, 4F, *ortho*-F), −138.34 (brs, 4F, *ortho*-F), −138.98 (brs, 4F, *ortho*-F), −149.89 (t, J=20.7 Hz, 2F, *para*-F), −150.15 (t, J=20.7 Hz, 2F, *para*-F), −150.26 (s, 2F, *b*-F), −151.69 (s, 2F, *b*-F), −152.27 (t, J=20.7 Hz, 2F, *para*-F), −159.42 (brs, 4F, *meta*-F), −160.31 (t, J=17.3 Hz, 4F, *meta*-F), and −161.24 ppm (m, 4F, *meta*-F); UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=310 (34000), 378 (33000), 593 (160000), 766 (12000), 854 (7300), 885 (6300) and 1013 nm (1300); HRMS (ESI-TOF, positive) calcd. for $C_{66}H_{13}F_{34}N_6$:1535.0653 $[M+H]^+$; found 1535.0666.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-5-hydro-2,3,17,18-tetrabromohexaphyrin(1.1.1.1.1.1) (**8a**)*

$NaBH_4$ (38 mg, 1.0 mmol) was added to a solution of **7a** (8.7 mg, 5 μmol) in CH_2Cl_2/MeOH (10 mL, 10:1), and the resulting solution was stirred at room temperature for 1 h under N_2 atmosphere. The reaction was quenched by addition of water, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. The crude product was purified by column chromatography using (CH_2Cl_2/*n*-hexane 1:2) to give a red fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave violet crystals of **8a** (3.7 mg, 42 %). Single crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of *n*-hexane into a solution of **8a** in CH_2Cl_2. ^{1}H NMR (600.17 MHz, $CDCl_3$, −60 °C) (two diastereomers): δ=11.24 (s, 1H, NH), 10.68 (s, 1H, NH), 10.53 (s, 1H, NH), 10.41 (s, 1H, NH), 8.40 (s, 1H, NH), 8.08 (s, 1H, NH), 7.92 (s, 1H, NH), 7.89 (s, 1H, NH), 7.74 (s, 1H, NH), 7.65 (s, 1H, NH), 6.85 (m, 1H, β-H), 6.79 (m, 1H, β-H), 6.72 (m, 1H, β-H), 6.70 (m, 1H, β-H), 6.61 (m, 1H, β-H), 6.56 (m, 3H, β-H), 6.44 (d, J=5.5 Hz, 1H, β-H), 6.40 (d, J=5.5 Hz, 1H, β-H), 6.22 (d, J=5.5 hz, 1H, β-H), 6.15 (d, J=5.5 Hz, 1H, β-H), 6.07 (m, 1H, β-H), 5.82 (m, 1H, β-H), 5.62 (s, 1H, *meso*-H), 5.54 (m, 1H, β-H), and 5.47 ppm (m, 1H, β-H and *meso*-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, −60 °C) (two diastereomers): δ=−135.43 (d, J=24.2 Hz, 1F, *ortho*-F), −135.65 (d, J=24.2 Hz, 1F, *ortho*-F), −135.78 (d, J=24.2 Hz, 1F, *ortho*-F), −135.95 (d, J=24.2 Hz, 1F, *ortho*-F), −136.46 (d, J=24.2 Hz, 1F, *ortho*-F), −136.93 (d, J=24.2 Hz, 1F, *ortho*-F), −138.03 (d, J=20.7 Hz, 1F, *ortho*-F), −138.17 (d, J=24.2 Hz, 1F, *ortho*-F), −138.69 (m, 1F, *ortho*-F), −138.84 (m, 1F, *ortho*-F), −139.23 (d, J=24.2 Hz, 1F, *ortho*-F), −139.58 (d, J=24.2 Hz, 1F, *ortho*-F), −139.75 (d, J=24.2 Hz, 1F, *ortho*-F), −140.22 (d, J=20.7 Hz, 1F, *ortho*-F), −140.20 (m, 2F, *ortho*-F), −140.92 (m, 4F, *ortho*-F), −141.27 (m, 1F, *ortho*-F), −141.41 (m, 1F, *ortho*-F), −141.66 (m, 1F, *ortho*-F), −145.23 (d, J=24.2 Hz, 1F, *ortho*-F), −149.06 (m, 1F, *para*-F), −149.42 (m, 1F, *para*-F), −149.60 (m, 1F, *para*-F), −149.84 (m, 1F, *para*-F), −151.38 (m, 1F, *para*-F), −151.67 (m, 3F, *para*-F), −152.14 (m, 3F, *para*-F), −152.40 (m, 1F, *para*-F), −156.90 (m, 1F, *meta*-F), −157.96 (m, 2F, *meta*-F), −158.26 (m, 3F, *meta*-F), −158.89 (m, 1F, *meta*-F), −159.36 (m, 4F, *para*-F), −159.68 (m, 1F, *meta*-F), −159.93 (m, 1F, *meta*-F), −160.49 (m, 1F, *meta*-F), and −160.64 to −161.11 ppm (m, 10F, *meta*-F); UV/vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=385 (23000), 441 (40000), 516 (41000), 555 (44000), and 923 nm (13000); HRMS (ESI-TOF, negative) calcd. for $C_{66}H_{13}Br_4F_{30}N_6$: 1778.7434 $[M-H]^-$; found 1778.7437.

*5,10,15,20,25,30-Hexakis(pentafluorophenyl)-5-hydro-2,3,17,18-tetrachlorohexaphyrin(1.1.1.1.1.1) (**8b**)*

$NaBH_4$ (38 mg, 1.0 mmol) was added to a solution of **7b** (8.0 mg, 5 μmol) in CH_2Cl_2/MeOH, and the resulting solution was stirred at room temperature for 1 h under N_2 atmosphere. The reaction was quenched by addition of water, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. The crude product was purified by column chromatography using (CH_2Cl_2/*n*-hexane 1:2) to give a red fraction. Recrystallization from CH_2Cl_2 and *n*-hexane gave violet crystals of **8a** (3.6 mg, 45 %). ^{1}H NMR (600.17 MHz, $CDCl_3$, −60 °C) (diastereomer 1): δ=11.08 (s, 1H, NH),

10.63 (s, 1H, NH), 8.14 (s, 1H, NH), 7.90 (s, 1H, NH), 7.66 (s, 1H, NH), 6.83 (m, 1H, β-H), 6.69 (m, 1H, β-H), 6.63 (m, 1H, β-H), 6.55 (m, 1H, β-H), 6.44 (d, J=5.5 Hz, 1H, β-H), 6.23 (d, J=5.5 hz, 1H, β-H), 6.07 (m, 1H, β-H), 5.83 (m, 1H, β-H) and 5.67 ppm (s, 1H, *meso*-H); (diastereomer 2) : δ=10.56 (s, 1H, NH), 10.50 (s, 1H, NH), 7.94 (s, 1H, NH), 7.86 (s, 1H, NH), 7.76 (s, 1H, NH), 6.79 (m, 1H, β-H), 6.67 (m, 1H, β-H), 6.59 (m, 1H, β-H), 6.55 (m, 1H, β-H), 6.39 (d, J=5.5 Hz, 1H, β-H), 6.16 (d, J=5.5 Hz, 1H, β-H), 5.55 (m, 1H, β-H), and 5.51 ppm (m, 2H, β-H and *meso*-H); ^{19}F NMR (564.73 MHz, $CDCl_3$, −60 °C) (diastereomer 1): δ=−136.38 (d, J=20.7 Hz, 1F, *ortho*-F), −138.34 (d, J=24.2 Hz, 1F, *ortho*-F), −139.10 (m, 1F, *ortho*-F), −139.80 (m, 1F, *ortho*-F), −140.87 (m, 4F, *ortho*-F), −141.06 (m, 2F, *orhot*-F), −141.28 (m, 1F, *ortho*-F), −145.10 (m, 1F, *ortho*-F), −149.34 (m, 1F, *para*-F), −149.50 (m, 1F, *para*-F), −152.12 (m, 3F, *para*-F), −152.41 (m, 1F, *para*-F), −156.89 (m, 1F, *meta*-F), −158.04 (m, 1F, *meta*-F), −158.30 (m, 1F, *meta*-F), −159.27 (m, 1F, *meta*-F), −159.42 (m, 1F, *meta*-F), −159.95 (m, 1F, *meta*-F) and −160.7 to −160.9 ppm (m, 6F, *meta*-F); (diastereomer 2): δ=−135.62 (m, 1F, *ortho*-F), −135.88 (m, 2F, *ortho*-F), −136.93 (d, J=20.7 Hz, 1F, *ortho*-F), −138.19 (d, J=20.7 Hz, 1F, *ortho*-F), −138.97 (m, 1F, *ortho*-F), −139.38 (m, 1F, *ortho*-F), −139.81 (m, 1F, *ortho*-F), −140.37 (d, J=20.7 Hz, 1F, *ortho*-F), −140.87 (m, 1F, *ortho*-F), −141.06 (m, 1F, *ortho*-F), −141.64 (m, 1F, *ortho*-F), −149.00 (m, 1F, *para*-F), −149.77 (m, 1F, *para*-F), −151.42 (m, 1F, *para*-F), −151.58 (m, 1F, *para*-F), −151.73 (m, 1F, *para*-F), −152.13 (m, 1F, *para*-F), −157.92 (m, 1F, *meta*-F), −158.31 (m, 1F, *meta*-F), −158.79 (m, 1F, *meta*-F), −159.27 (m, 2F, *meta*-F), −159.58 (m, 1F, *meta*-F), −160.48 (m, 1F, *meta*-F), and −160.7~-160.9 ppm (m, 5F, *meta*-F); UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$)=387 (24000), 436 (41000), 515 (42000), 552 (44000), and 916 nm (13000); HRMS (ESI-TOF, negative) calcd. for $C_{66}H_{13}Cl_4F_{30}N_6$: 1600.9469 $[M-H]^-$; found 1600.9457.

Acknowledgements

This work was supported by Grants-in-Aid (No. 22245006 (A) and 20108001 "pi-Space") for Scientific Research from MEXT. T.H. acknowledges a JSPS Fellowship for Young Scientists.

[1] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267–2340; b) T. D. Lash, *Angew. Chem.* **2000**, *112*, 1833–1837; *Angew. Chem. Int. Ed.* **2000**, *39*, 1763–1767; c) H. Furuta, H. Maeda, A. Osuka, *Chem. Commun.* **2002**, 1795–1804; d) J. L. Sessler, D. Siedel, *Angew. Chem.* **2003**, *115*, 5292–5333; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134–5175; e) T. K. Chandrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676–691; f) M. Stępień, N. Sprutta, L. Latos-Grażyński, *Angew. Chem.* **2011**, *123*, 4376–4430; *Angew. Chem. Int. Ed.* **2011**, *50*, 4288–4340; g) S. Saito, A. Osuka, *Angew. Chem.* **2011**, *123*, 4432–4464; *Angew. Chem. Int. Ed.* **2011**, *50*, 4342–4373; h) S. Saito, A. Osuka, *Chem. Commun.* **2011**, *47*, 4330–4339.

[2] a) S. Shimizu, J.-Y. Shin, H. Furuta, R. Ismael, A. Osuka, *Angew. Chem.* **2003**, *115*, 82–86; *Angew. Chem. Int. Ed.* **2003**, *42*, 78–82; b) S. Mori, K. S. Kim, Z. S. Yoon, S. B. Noh, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 11344–11345; c) T. Koide, K. Youfu, S. Saito, A. Osuka, *Chem. Commun.* **2009**, 6047–6049; d) T. Koide, A. Osuka, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 877–879; e) T. Higashino, A. Osuka, *Chem. Sci.* **2013**, *4*, 1087–1091.

[3] a) T. Takeuchi, H. B. Gray, W. A. Goddard III., *J. Am. Chem. Soc.* **1994**, *116*, 9730–9732; b) P. Ochsenbein, K. Ayougou, D. Mandon, J. Fischer, R. Weiss, R. N. Austin, K. Jayaraj, A. Gold, J. Terner, J. Fajer, *Angew. Chem.* **1994**, *106*, 355–357; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 348–350; c) G. A. Spyroulias, A. P. Despotopoulos, C. P. Raptopoulou, A. Terzis, D. de Montauzon, R. Poilblanc, A. G. Coutsolelos, *Inorg. Chem.* **2002**, *41*, 2648–2659.

[4] J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568–13579.

[5] a) R. B. Woodward, *Angew. Chem.* **1960**, *72*, 651–662; b) R. B. Woodward, *Ind. Chim. Belge* **1962**, *27*, 1293–1308.

[6] a) J.-W. Ka, C.-H. Lee, *Tetrahedron Lett.* **2001**, *42*, 4527–4529; b) A. J. Pistner, G. P. A. Yap, J. Rosenthal, *J. Phys. Chem. C* **2012**, *116*, 16918–16924.

[7] a) T. D. LeSaulnier, B. W. Graham, G. R. Geier III., *Tetrahedron Lett.* **2005**, *46*, 5633–5637; b) A. Y. O'Brien, J. P. McGann, G. R. Geier III., *J. Org. Chem.* **2007**, *72*, 4084–4092.

[8] a) S. Sugimoto, *J. Chem. Soc. Dalton Trans.* **1982**, 1169–1171; b) H. Segawa, R. Azumi, T. Shimidzu, *J. Am. Chem. Soc.* **1992**, *114*, 7564–7565; D. T. Gryko, B. Koszarna, *Eur. J. Org. Chem.* **2005**, 3314.

[9] a) J. Setsune, M. Ikeda, T. Iida, T. Kitao, *J. Am. Chem. Soc.* **1988**, *110*, 6572–6574; b) J. Setsune, Y. Ishimaru, T. Kitao, *Chem. Lett.* **1990**, 1351–1354; c) J. Setsune, H. Yamaji, T. Kitao, *Tetrahedron Lett.* **1990**, *31*, 5057–5060.

[10] a) B. Krattinger, H. J. Callot, *Chem. Commun.* **1996**, 1341–1342; b) R. Ruppert, C. Jeandon, A. Sgambati, H. J. Callot, *Chem. Commun.* **1999**, 2123–2124; c) B. Krattinger, H. J. Callot, *Eur. J. Org. Chem.* **1999**, 1857–1867.

[11] a) K. Youfu, A. Osuka, *Tetrahedron Lett.* **2006**, *47*, 1381–1384; b) M. Inoue, A. Osuka, *Angew. Chem.* **2010**, *122*, 9678–9681; *Angew. Chem. Int. Ed.* **2010**, *49*, 9488–9491; c) T. Higashino, A. Osuka, *Chem. Sci.* **2012**, *3*, 103–107.

[12] a) T. Miura, T. Higashino, S. Saito, A. Osuka, *Chem. Eur. J.* **2010**, *16*, 55–59; b) T. Higashino, J. M. Lim, T. Miura, S. Saito, J.-Y. Shin, D. Kim, A. Osuka, *Angew. Chem.* **2010**, *122*, 5070–5074; *Angew. Chem. Int. Ed.* **2010**, *49*, 4950–4954.

[13] a) J. S. Reddy, S. Mandal, V. G. Anand, *Org. Lett.* **2006**, *8*, 5541–5543; b) J. S. Reddy, V. G. Anand, *J. Am. Chem. Soc.* **2009**, *131*, 15433–15439.

[14] B. L. Bray, P. H. Mathies, R. Naef, D. R. Solas, T. T. Tidwell, D. R. Artis, J. M. Muchowski, *J. Org. Chem.* **1990**, *55*, 6317–6328.

[15] a) P. Anzenbacher, Jr., A. C. Try, H. Miyaji, K. Jursíková, V. M. Lynch, M. Marquez, J. L. Sessler, *J. Am. Chem. Soc.* **2000**, *122*, 10268–10272; b) J. L. Sessler, P, Anzenbacher, Jr., J. A. Shriver, K. Jursíková, V. M. Lynch, M. Marquez, *J. Am. Chem. Soc.* **2000**, *122*, 12061–12062; c) J. L. Sessler, W.-S. Cho, D. E. Gross, J. A. Shriver, V. M. Lynch, M. Marquez, *J. Org. Chem.* **2005**, *70*, 5982–5986.

[16] a) H.-Y. Liu, T.-S. Lai, L.-L. Yeung, C. K. Chang, *Org. Lett.* **2003**, *5*, 617–620; b) E. Steene, A. Dey, A. Ghosh, *J. Am. Chem. Soc.* **2003**, *125*, 16300–16309; c) D. K. Dogutan, R. McGuire, Jr., D. G. Nocera, *J. Am. Chem. Soc.* **2011**, *133*, 9178–9180.

[17] a) H. Fischer, K. Gangle, *Z. Phys. Chem.* **1941**, *267*, 188–200; b) R. J. Motekaitis, D. H. Heinert, A. E. Martell, *J. Org. Chem.* **1970**, *35*, 2504–2511; c) J. Leroy, C. Wakselman, *Tetrahedron Lett.* **1994**, *35*, 8605–8608; d) E. K. Woller, V. V. Smirnov, S. G. DiMagno, *J. Org. Chem.* **1998**, *63*, 5706–5707.

[18] H. Mori, N. Aratani, A. Osuka, *Chem. Asian J.* **2012**, *7*, 1340–1346.

[19] a) Crystallographic data for **7a**: $C_{66}H_{12}Br_4F_{30}N_6 \cdot 0.6(C_3H_8O) \cdot 0.4(C_2H_4Cl_2)$, M_r=1854.22; monoclinic; space group $P2_1/c$ (No.14), a=12.6023(4), b=13.5758(5), c=38.0553(14) Å; β=90.5212(19)°; V=6510.5(4) Å^3; ρ_{calcd}=1.892 g cm^{-3}; Z=4; R_1=0.0767 [$I>2.0\sigma(I)$], wR_2=0.2401 (all data), GOF=1.022; b) Crystallographic data for **8a**: $C_{66}H_{14}Br_4F_{30}N_6 \cdot C_6H_{14} \cdot 2.55(CH_2Cl_2)$, M_r=2083.13; monoclinic; space group $P2_1/c$ (No.14), a=18.4086(3), b=14.7578(3), c=30.0587(6) Å; β=92.4140(8)°; V=8158.8(3) Å^3; ρ_{calcd}=1.696 g cm^{-3}; Z=4; R_1=0.0961 [$I>2.0\sigma(I)$], wR_2=0.3069 (all data), GOF=1.065. CCDC 931825 (**7a**) and CCDC 931826 (**8a**) 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.

[20] R. Taniguchi, S. Shimizu, M. Suzuki, J.-Y. Shin, H. Furuta, A. Osuka, *Tetrahedron Lett.* **2003**, *44*, 2505–2507.

Received: April 8, 2013
Published online: ■■ ■■, 0000