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Conformational Control of [26]Hexaphyrins(1.1.1.1.1.1) by *meso*-Thienyl Substituents

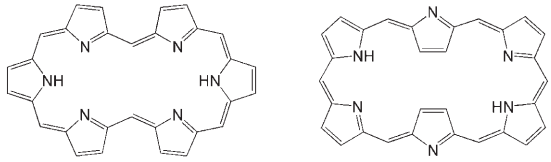
Masaaki Suzuki and Atsuhiro Osuka*[a]

Abstract: Conformational preference and chemical stability of *meso*-aryl-substituted [26]hexaphyrins(1.1.1.1.1.1) ([26]ArH) depend upon *meso*-aryl substituents. Although only a planar and rectangular conformation (type-II conformation) has been identified for [26]ArH so far, we have demonstrated here that a different conformation with all the pyrroles pointing inward (type-I conformation) is preferred for [26]ArH (**7** and **11**-I) bearing small 2-thienyl or 3-thineyl substituents at 15- and 30-positions. Both type-I and type-II [26]ArH exhibit diatropic ring currents, reflecting aromatic character. Type-I [26]ArH, such as **7** and **11**-I, have been shown to serve as an effective ligand for Pd^{II} ions to provide bis-Pd^{II} complexes **12** and **13** with N_3C_1 coordination through facile C–H bond activation.

Keywords: C–H activation · palladium · porphyrinoids · structure elucidation

Introduction

Recently, increasing attention has been focused on expanded porphyrins, which have a conjugated pyrrolic macrocycle larger than porphyrins themselves, in light of their unique chemical, optical, and electrochemical properties, as well as their rich coordination chemistry.[1] Among these, hexaphyrins(1.1.1.1.1.1) possess a unique position in view of their structural and functional diversities that are more or less analogous to those of porphyrins. In 1993, Gossauer et al. reported the synthesis of unstable β-alkyl substituted hexaphyrin(1.1.1.1.1.1) **1** as the first example. On the basis of its ^{1}H NMR data, **1** was concluded to be aromatic with a type-I conformation, in which all the pyrrolic rings took inward orientation.[2] In 1997, Dolphin et al. reported *meso*-hexaphenyl-substituted hexaphyrin(1.1.1.1.1.1) **2**, which was particularly unstable and precluded its full characterization.[3] In 1999, Cavaleiro et al. reported *meso*-hexakis(pentafluorophenyl)-substituted hexaphyrin(1.1.1.1.1.1) **3** in about 1% yield, which was shown to be a stable aromatic macrocycle with a conjugated 26π-network that was interconvertible to its reduced 28π-congener.[4] In the meanwhile, we have synthesized *meso*-aryl substituted [26]hexaphyrins(1.1.1.1.1.1) ([26]ArH) in better yields,[8] and explored their unique reactivities,[5] diverse metalation behaviors,[6] and extremely large two-photon absorption cross sections.[7] The strong aromatic character of **3** relies on the almost planar and rectangular conformation with two inverted pyrroles (type-II conformation), which is the a sole stable conformation so far identified for [26]ArH. In this paper, we report that introduction of small aryl substituents at both 15- and 30-positions leads to stable type-I [26]ArH, which can serve as an effective binuclear ligand to provide bis-Pd^{II}-complexes through double C–H bond activation.



Type I Type II

Results and Discussion

First, hexaphyrins **4** and **6** bearing two or three *meso*-phenyl substituents were prepared from tripyrrane or dipyrromethane precursor according to our synthetic protocol.[5b,8c]

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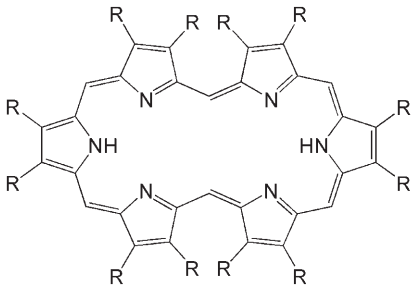
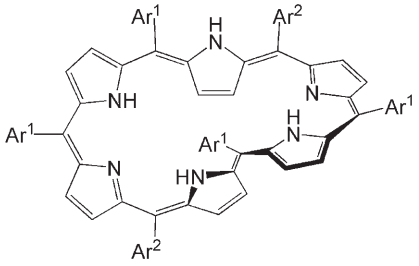
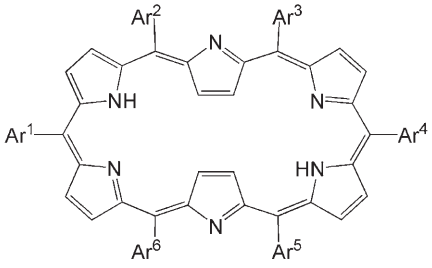


1: R = CH_3, $(CH_2)_2CO_2CH_3$



8: Ar^1 = pentafluorophenyl, Ar^2 = 2-thienyl



2: $Ar^1 = Ar^2 = Ar^3 = Ar^4 = Ar^5 = Ar^6$ = phenyl
3: $Ar^1 = Ar^2 = Ar^3 = Ar^4 = Ar^5 = Ar^6$ = pentafluorophenyl
4: $Ar^1 = Ar^4$= phenyl,
$Ar^2 = Ar^3 = Ar^5 = Ar^6$ = pentafluorophenyl
5: $Ar^2 = Ar^5$= phenyl,
$Ar^1 = Ar^3 = Ar^4 = Ar^6$ = pentafluorophenyl
6: $Ar^1 = Ar^3 = Ar^5$ = phenyl,
$Ar^2 = Ar^4 = Ar^6$ = pentafluorophenyl
7: $Ar^1 = Ar^4$ = 2-thienyl,
$Ar^2 = Ar^3 = Ar^5 = Ar^6$ = pentafluorophenyl
9: $Ar^1 = Ar^3 = Ar^5$ = 2-thienyl,
$Ar^2 = Ar^4 = Ar^6$ = pentafluorophenyl
10: $Ar^1 = Ar^4$ = 3-methyl-2-thienyl,
$Ar^2 = Ar^3 = Ar^5 = Ar^6$ = pentafluorophenyl
11: $Ar^1 = Ar^4$ = 3-thienyl,
$Ar^2 = Ar^3 = Ar^5 = Ar^6$ = pentafluorophenyl

Type-II conformation of **4** has been indicated from its ^{1}H NMR spectral data and confirmed by X-ray crystallographic analysis (Figure 1). Just after the preparation, a minor conformer (hexaphyrin **5**) was detected in the ^{1}H NMR spectrum of a hexaphyrin fraction separated by silica gel column chromatography, but was smoothly converted to **4** upon standing. Hexaphyrin **6** has been also shown to take the similar type-II conformation on the basis of its ^{1}H NMR and absorption spectrum, but was considerably unstable in solution under aerobic conditions and changed to intractable material within several hours, in contrast to chemical stability of **4**. These results suggested that 1) an electron- deficient pentafluorophenyl group favors *meso*-positions on the long side of rectangle and 2) [26]ArH becomes unstable when a sterically uncongested phenyl group occupies the *meso*-positions of the long side.

Next, hexaphyrins **7** and **9** bearing two or three *meso*-2-thienyl substituents were prepared in 35% and 7% yields from appropriate precursors.[5b,8c] Hexaphyrin **7** displays a less intense Soret-like absorption band at 616 nm in its absorption spectrum compared with that of **3** (Figure 2) and the signals due to the peripheral pyrrolic β-protons are found at $\delta = 7.38$, 7.72, and 8.16 ppm in the ^{1}H NMR spectrum; these results are also quite different from those found for **3**. Type-I structure of **7** has been revealed by X-ray diffraction analysis, in which all the pyrroles take inward orientation and the two tripyrrodimethene moieties are bridged by the 2-thienyl-substituted methine carbon atoms (Figure 3). Overall, the macrocycle is rather planar with a small mean plane deviation of 0.268 Å for the 36 core atoms. The 2-thienyl groups are positioned above and below the macrocycle with relatively small dihedral angles (ca. 8.6°) toward the connecting dipyrromethene segment, hence avoiding steric congestion between the two 2-thienyl groups. The 2-thienyl protons are upfield shifted to $\delta = 4.55$, 4.92, and 5.35 ppm, indicating a diatropic ring cur-

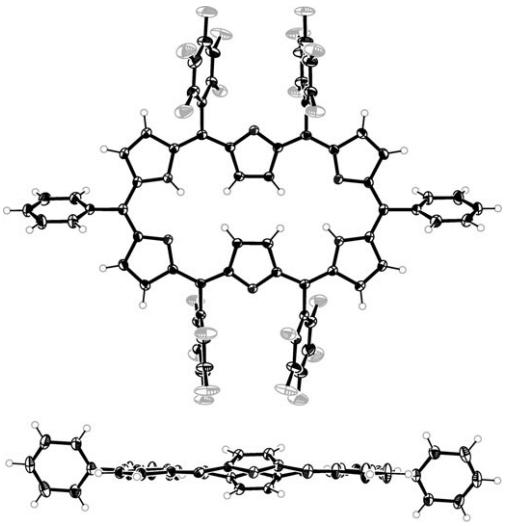


Figure 1. Crystal structure of **4**. Top: top view. Bottom: side view. Pentafluorophenyl groups are omitted for clarity in the side view. Thermal ellipsoids are scaled to the 50% probability level.

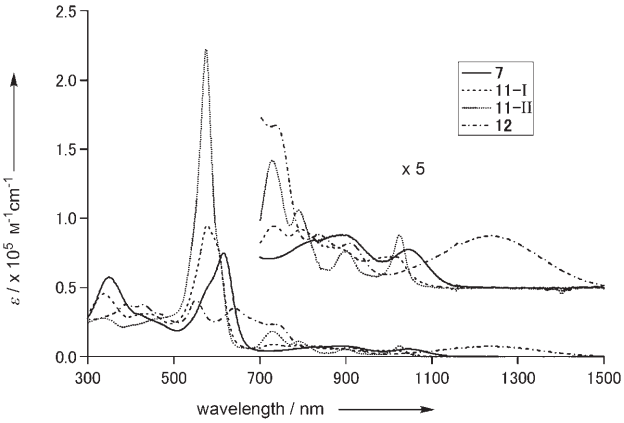


Figure 2. UV/Vis absorption spectra of **7**, **11**, and **12** in CH_2Cl_2.

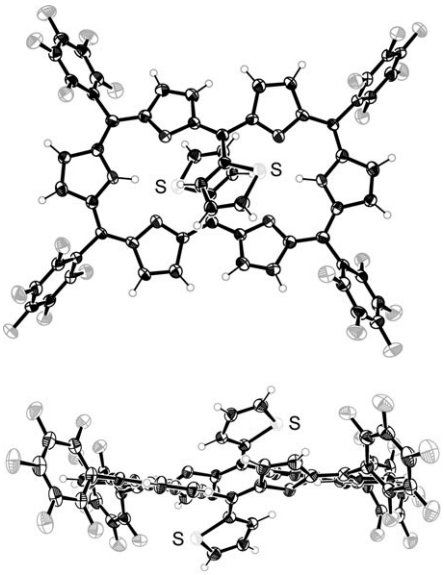


Figure 3. Crystal structure of **7**. Top: top view. Bottom: side view. Thermal ellipsoids are scaled to the 50% probability level.

rent of the [26]hexaphyrin macrocycle that is estimated to be slightly weaker than that of **3**, as judged from the smaller downfield shifts of the peripheral β-protons. The hexaphyrin **7** was quantitatively reduced with $NaBH_4$ to [28]hexaphyrin **8**, which displayed a very broad ^{1}H NMR spectrum, probably reflecting considerable conformational flexibility. X-ray crystallographic analysis has revealed a highly distorted structure of **8** (Figure 4). Therefore, it may be concluded that the incorporation of two 2-thienyl groups at 15- and 30-positions also influences a stable conformation of [28]hexaphyrin. On the other hand, hexaphyrin **9** is considerably unstable probably due to its type-II conformation with small 2-thienyl groups at the long side *meso*-position.

To examine more subtle steric effects, we prepared **10** and **11** bearing 3-methyl-2-thienyl and 3-thienyl *meso*-substituents, respectively. The type-II conformation of **10** was indicated by its ^{1}H NMR and absorption spectra, and has been confirmed by X-ray diffraction analysis (Figure 5).[9] On the other hand, hexaphyrin **11** exhibited a unique feature; intact **11** as prepared took a type- II conformation (**11**-II), but was changed to a type-I conformation (**11**-I) upon heating at 50 °C in $CHCl_3$, and an equilibrated mixture (**11**-I/**11**-II = 7:1) was formed after 3 h (Scheme 1). This fact allowed an estimation of the energy difference (1.2 kcal mol^{-1}) between the two conformers. Importantly the two conformers were isolated in a pure form at room temperature and structurally well characterized (Figures 6 and 7). In line with these structural assignments, the two isomers display absorption spectra that are characteristic of type-I and type-II conformations, respectively (Figure 2). From the examination of the temperature dependence of the transformation from **11**-II to **11**-I by ^{1}H NMR measurements, the activation barrier has been determined to be 8.7 kcal mol^{-1}. Effective intramolecular hydrogen-bonding interactions favor **11**-I, but steric congestion between the *meso*-aryl substituents at the 5- and 20-positions disfavors **11**-I with respect to **11**-II. It is thus conceivable that bulky substituents at the inward *meso*-positions in type-I conformation cause substantial steric repulsion, forcing conformational change to a type-II [26]ArH.

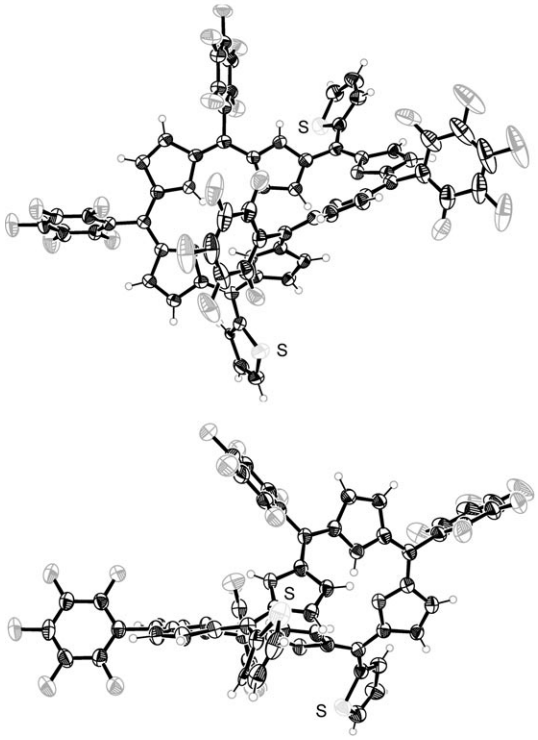


Figure 4. Crystal structure of **8**. Top: top view. Bottom: side view. Thermal ellipsoids are scaled to the 50% probability level.

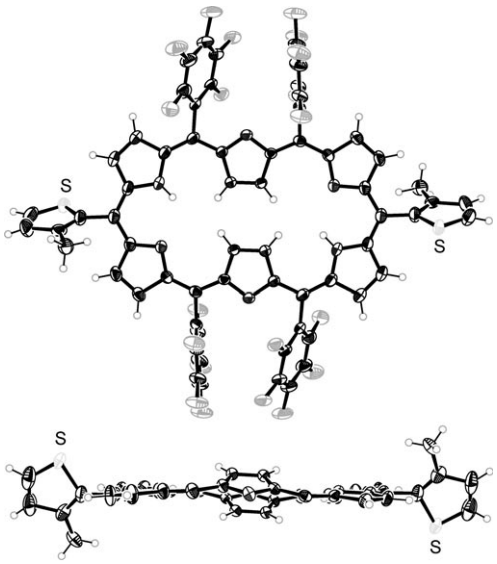
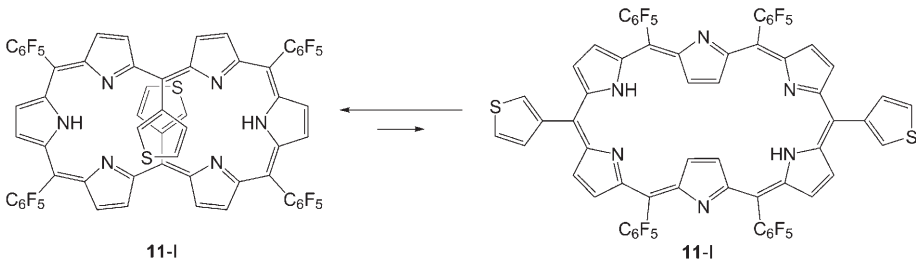


Figure 5. Crystal structure of **10**. Top: top view. Bottom: side view. Pentafluorophenyl groups are omitted for clarity in the side view. Thermal ellipsoids are scaled to the 50% probability level.



Scheme 1. Interconversion between **11**-I and **11**-II.

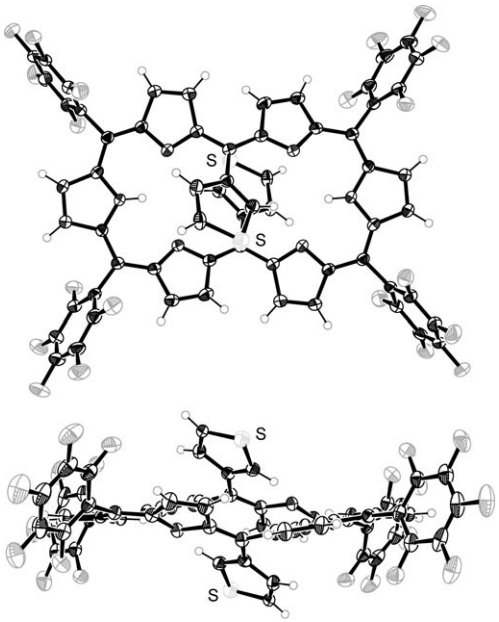


Figure 6. Crystal structure of **11**-I. Top: top view. Bottom: side view. Thermal ellipsoids are scaled to the 50% probability level.

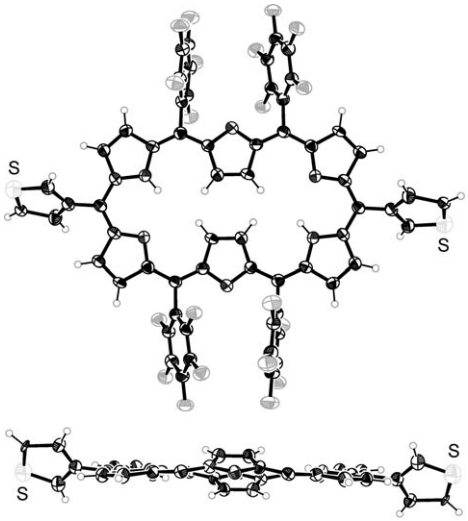


Figure 7. Crystal structure of **11**-II. Top: top view. Bottom: side view. Thermal ellipsoids are scaled to the 50% probability level.

Type-I hexaphyrin **7** can form a new bis-metalation products of [26]ArH (Scheme 2). Treatment of **7** with $Pd(OAc)_2$ in a mixture of methanol and CH_2Cl_2 caused smooth metalation within 20 min at room temperature to provide the bis-Pd^{II} complex **12** in 53% yield. The ^1H NMR spectrum of **12** exhibited considerably upfield shifted signals due to the 4- and 5-protons of the 2-thienyl group at $\delta = 2.69$ and 3.78 ppm, respectively, in addition to six doublets due to the peripheral β-protons in a range of $\delta = 8.26$–9.76 ppm, hence indicating that the 3-positions of the thienyl groups were metalated through C–H bond cleavage. Eventually the structure has been unambiguously confirmed by X-ray diffraction analysis as shown in Figure 8, which reveals a C_2-symmetric novel

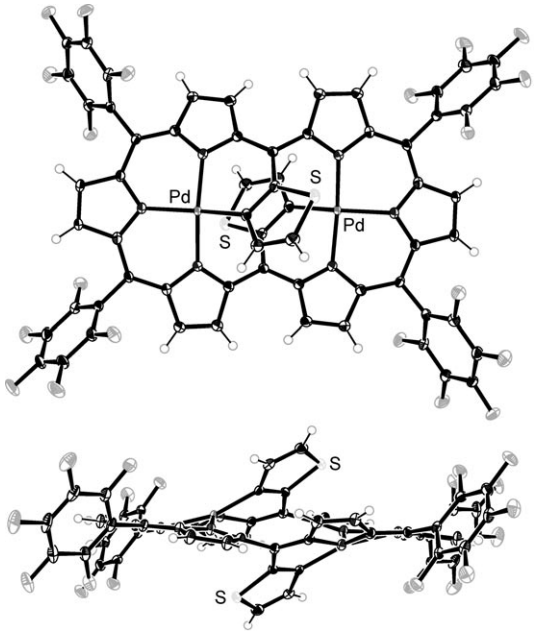
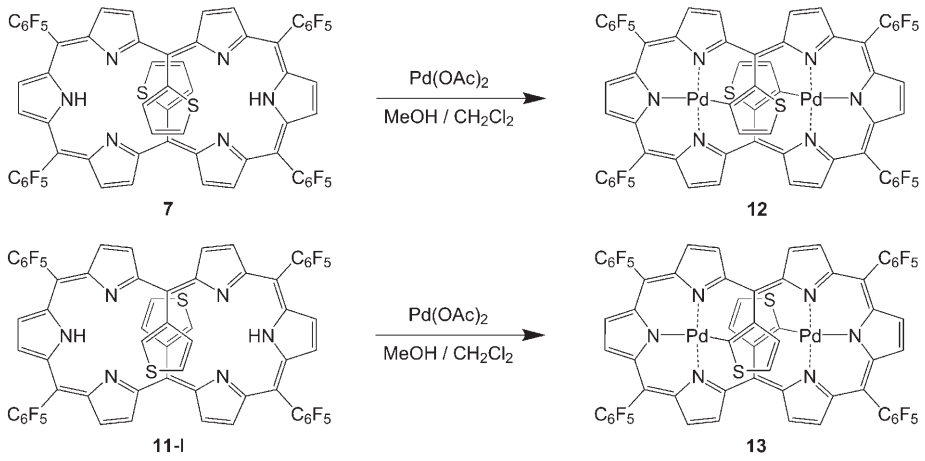


Figure 8. Crystal structure of **12**. Top: top view. Bottom: side view. Thermal ellipsoids are scaled to the 50% probability level.

coordination structure with a type-I conformation. Each Pd^{II} ion is bound with the three pyrrolic nitrogen atoms and the carbon atom of the thienyl group in a nearly square-planar fashion. The mean plane deviation of the 36 core atoms of the macrocycle is only 0.214 Å with a displacement of Pd^{II} ion by 0.491 Å above the mean plane. The coordination mode of **12** is reminiscent of those of N-confused porphyrins[1d] and other carbaporphyrins.[10] It is interesting to note that the Pd–C (1.97 Å) and averaged Pd–N (2.02 Å) distances of **12** are similar to those of N-confused porphyrin Pd complexes.[1d,11] Type-I hexaphyrin **11**-I also underwent similar Pd^{II} metalation, which proceeded even at −20 °C to pro-



Scheme 2. Bis-palladation of **7** to **12** and **11**-I to **13**.

vide **13** in 63% yield, since the C–H bond cleavage occurred at the intrinsically active α-position of the thienyl group.[12] The structure of **13** has been revealed by X-ray analysis (Figure 9). Interestingly, both complexes **12** and **13** exhibit considerably broadened absorption spectra with a broad band at low energy (1244 and 1191 nm for **12** and **13**, respectively, Figure 2).

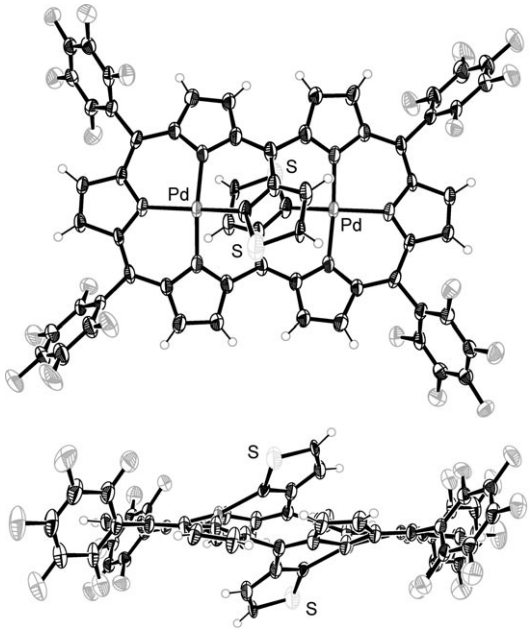


Figure 9. Crystal structure of **13**. Top: top view. Bottom: side view. Thermal ellipsoids are scaled to the 50% probability level.

Conclusion

In summary, there are at least two stable conformations for [26]ArH, type-I and type-II confirmations, which are delicately balanced by the steric factors of *meso*-aryl substituents. Hexaphyrins **7** and **11**-I are, to the best of our knowledge, the first type-I [26]ArH compounds, and it is only permitted for those bearing small aryl groups both at 15- and 30-positions, whereas type-II conformations are predominant for other [26]ArH compounds. The type-I compounds **7** and **11** have been demonstrated to serve as an effective ligand for Pd^{II} ions to provide complexes **12** and **13** through the facile C–H bond activation. Study on the metalation of other ions into these type-I [26]ArH compounds is worthy of further investigation.

Experimental Section

General: All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. ^{1}H NMR spectra were recorded on a JEOL ECA-600 spectrometer, (operating as 600.17 MHz for ^{1}H and 564.73 MHz for ^{19}F) using the residual solvent in $CDCl_3$ and CD_2Cl_2 as the internal reference for ^{1}H ($\delta = 7.26$ and 5.30 ppm, respectively) and hexafluorobenzene as external reference for ^{19}F ($\delta = -162.9$ ppm). Spectroscopic grade CH_2Cl_2 was used as solvents for all spectroscopic studies. UV/Visible absorption was recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a BRUKER microTOF by using positive mode ESI-TOF method in acetonitrile. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-400). CCDC-607198 (**4**), CCDC-606795 (**7**), CCDC-606796 (**8**), CCDC-606797 (**10**), CCDC-606798 (**11**-II), CCDC-606799 (**11**-II), CCDC-606801 (**12**), CCDC-607199 (**13**) 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.

[26]Hexaphyrins: Methanesulfonic acid (2.5 M diluted with CH_2Cl_2, 12.5 μl) was added to a solution of aldehyde (0.50 mmol) and 5,10-bis-(pentafluorophenyl) tripyrrane (278 mg, 0.5 mmol) in CH_2Cl_2 (22.2 mL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 500 mg) was added. After further stirring for 1 h at room temperature, the resulting solution was passed through a short basic-alumina column with MeOH/CH_2Cl_2 (1:9) and solvent was removed by a rotary evaporator. The residual mixture was purified by silica gel column chromatography. Appropriate fractions were collected, then evaporated to dryness. Recrystallization from CH_2Cl_2/MeOH afforded the target [26]hexaphyrin.

[28]Hexaphyrins: MeOH was added to a solution of [26]hexaphyrin (0.0020 mmol) and excess $NaBH_4$ (1.0 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred for 1 h and quenched with water. The organic phase was successively washed with water and brine, then dried over Na_2SO_4. Removal of solvent gave [28]hexaphyrin in an almost quantitative yield.

Pd complexes: MeOH (3 mL) was added to a solution of [26]hexaphyrin (**7** or **11**-I, 30.0 mg, 23.2 mmol) and $Pd(OAc)_2$ in CH_2Cl_2 (9 mL), and the resulting solution was stirred for 20 min at room temperature under a nitrogen atmosphere. Reaction mixture was passed through a short alumina column with CH_2Cl_2. After removal of solvent, the residual mixture was separated by silica gel column chromatography with CH_2Cl_2/hexane (3:7) as an eluent. The appropriate fraction was collected and evaporated, followed by recrystallization from CH_2Cl_2/MeOH, giving Pd complex.

5,20-Bis(phenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (4): The eluent used for silica gel column chromatography was CH_2Cl_2/hexane (3:7). Purple solution, greenish solid, yield 7.2%; ^{1}H NMR ($CDCl_3$): $\delta = -2.63$ (s, 4H; inner β-H), −2.19 (br, 2H; NH), 7.92 (m, 6H; phenyl), 8.39 (m, 4H; phenyl), 9.21 (d, $J = 4.4$ Hz, 4H; outer β-H), 9.39 ppm (d, $J = 4.8$ Hz, 4H; outer β-H); ^{19}F NMR ($CDCl_3$): $\delta = -163.25$ (m, 8F; *meta*-F), −153.40 (m, 4F; *para*-F), −136.93 ppm (d, $J = 26.3$ Hz, 8F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1020 (7900), 892 (6900), 784 (12000), 725 (20000), 573 nm (210000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{66}H_{25}F_{20}N_6$ ($[M+H]^+$): 1281.1816, found: 1281.1908 (100%); crystal data: $C_{66}H_{24}F_{20}N_6 \cdot 2\,C_4H_8O_2$, $M_r = 1426$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.518(4)$, $b = 11.348(3)$, $c = 19.583(5)$ Å, $\beta = 97.49(1)°$, $V = 3199(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.513$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.070$ [$I > 2\sigma(I)$], $R_W = 0.205$ (all data), GOF = 1.053. Crystals were grown from AcOEt/*n*-hexane at −20 °C.

5,20-Bis(2-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (7): The eluent used for silica gel column chromatography was CH_2Cl_2/hexane (3:7). Greenish blue solution, reddish solid, yield 35%; ^{1}H NMR ($CDCl_3$): $\delta = 4.55$ (d, $J = 4.0$ Hz, 2H; thienyl), 4.92 (t, $J = 4.4$ Hz, 2H; thienyl), 5.35 (d, $J = 4.8$ Hz, 2H; thienyl), 7.38 (s, 4H; β-H), 7.72 (s, 4H; outer β-H), 8.16 ppm (d, $J = 3.8$ Hz, 4H; β-H); ^{19}F NMR ($CDCl_3$): $\delta = -160.81$ (br 4F; *meta*-F), −160.61 (br, 4F; *meta*-F), −151.53 (t, $J = 17.6$ Hz, 4F; *para*-F), −137.47 (d, $J = 26.3$ Hz, 4F; *ortho*-F), −136.97 ppm (d, $J = 35.0$ Hz, 4F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1044 (5500), 892 (7700), 616 (75000), 349 nm (57000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{62}H_{21}F_{20}N_6S_2$ ($[M+H]^+$): 1293.0944; found: 1293.0946 (100%); crystal data: $C_{62}H_{20}F_{20}N_6S_2$, $M_r = 1293$, monoclinic, space group $P2_1/n$ (No. 14), $a = 13.916(6)$, $b = 9.286(4)$, $c = 19.81(1)$ Å, $\beta = 103.89(2)°$, $V = 2484(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.728$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.070$ [$I > 3\sigma(I)$], $R_W = 0.192$ (all data), GOF = 0.999. Crystals were grown from $CHCl_3$/MeOH.

5,20-Bis(2-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[28]hexaphyrin (8): UV/Vis (CH_2Cl_2): λ_{max} (ε) = 885 (6800), 783 (10000), 621 (150000), 449 (28000), 405 (42000), 319 nm (28000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{62}H_{23}F_{20}N_6S_2$ ($[M+H]^+$): 1295.1101; found: 1295.1137 (100%); crystal data: $C_{62}H_{22}F_{20}N_6S_2 \cdot CH_2Cl_2$, $M_r = 1380$, monoclinic, space group $P2_1/n$ (No. 14), $a = 16.967(3)$, $b = 14.577(3)$, $c = 26.291(5)$ Å, $\beta = 106.816(6)°$, $V = 6225(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.472$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.0$ 98 [$I > 2\sigma(I)$], $R_W = 0.$ 314 (all data), GOF = 1.067. Crystals were grown from CH_2Cl_2/MeOH.

5,15,25-Tris(thienyl)-10,20,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (9): The eluent used for silica gel column chromatography was CH_2Cl_2/hexane (5:5). Blue solution, red solid, yield 6.6%; UV/Vis (CH_2Cl_2): $\lambda_{max} = 1064$, 837, 754, 590, 451, 421 nm; HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{60}H_{24}F_{15}N_6S_3$ ($[M+H]^+$): 1209.0980; found: 1209.0904 (100%).

5,20-Bis(3-methyl-2-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]-hexaphyrin (10): The eluent used for silica gel column chromatography was CH_2Cl_2/hexane (3:7). Purple solution, greenish solid, yield 23%; ^{1}H NMR ($CDCl_3$): $\delta = -2.54$ (s, 4H; inner β-H), −2.13 (br, 2H; NH), 2.33 (s, 3H; methyl), .38 (s, 3H; methyl), 7.46 (t, $J = 5.5$ Hz, 2H; thienyl), 7.91 (t, $J = 5.5$ Hz, 2H; thienyl), 9.27 (m, 4H; outer β-H), 9.36 ppm (d, $J = 4.6$ Hz, 4H; outer β-H); ^{19}F NMR ($CDCl_3$): $\delta = -163.21$ (m, 8F; *meta*-F), −153.31 (t, $J = 17.6$ Hz, 4F; *para*-F), −137.09 (d, $J = 26.3$ Hz, 4F; *ortho*-F), −136.88 (s, 4F; *ortho*-F), −136.79 ppm (d, $J = 17.6$ Hz, 4F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1028 (8900), 901 (5200), 787 (11000), 726 (24000), 576 nm (280000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{64}H_{25}F_{20}N_6S_2$ ($[M+H]^+$): 1321.1257; found: 1321.1262 (100%); crystal data: $C_{64}H_{24}F_{20}N_6S_2 \cdot 2\,C_4H_{16}O_2$, $M_r = 1497$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.290(5)$, $b = 9.286(4)$, $c = 19.81(1)$ Å, $\beta = 103.89(2)°$, $V = 2484(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.555$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.061$ [$I > 2\sigma(I)$], $R_W = 0.161$ (all data), GOF = 1.032. Crystals were grown from AcOEt/hexane.

5,20-Bis(3-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (11-II): The eluent used for silica gel column chromatography was CH_2Cl_2/hexane (5:5). Dark purple solution, greenish solid, yield 26%; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.52$ (s, 4H; inner β-H), −2.35 (br, 2H; NH), 7.93 (m, 2H; thienyl), 8.21 (m, 2H; thienyl), 8.27 (m, 2H; thienyl), 9.32 (d, $J = 4.6$ Hz, 4H; outer β-H), 9.37 ppm (d, $J = 4.6$ Hz, 4H; outer β-H); ^{19}F NMR ($CDCl_3$): $\delta = -163.24$ (s, 8F; *meta*-F), −153.36 (m, 4F; *para*-F), −136.96 ppm (d, $J = 17.6$ Hz, 8F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1024 (7600), 901 (5300), 789 (11000), 728 (18000), 575 (220000), 336 nm (28000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{62}H_{21}F_{20}N_6S_2$ ($[M+H]^+$): 1293.0944; found: 1293.0935 (100%); crystal data: $C_{62}H_{20}F_{20}N_6S_2 \cdot CH_2Cl_2$, $M_r = 1426$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.596(5)$, $b = 17.523(9)$, $c = 15.677(7)$ Å, $\beta = 98.99(2)°$, $V = 2875(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.647$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.101$ [$I > 2\sigma(I)$], $R_W = 0.325$ (all data), GOF = 1.091. Crystals were grown from CH_2Cl_2/MeOH at −20 °C.

5,20-bis(3-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin (11-I): The eluent used for silica gel column chromatography was CH_2Cl_2. Dark blue solution, reddish solid, yield 88%; ^{1}H NMR ($CDCl_3$): $\delta = 4.55$ (d, $J = 4.0$ Hz, 2H; thienyl), 4.92 (t, $J = 4.4$ Hz, 2H; thienyl), 5.35 (d, $J = 4.8$ Hz, 2H; thienyl), 7.38 (s, 4H; β-H), 7.72 (s, 4H; outer β-H), 8.16 ppm (d, $J = 3.8$ Hz, 4H; β-H); ^{19}F NMR ($CDCl_3$): $\delta = -160.81$ (br, 4F; *meta*-F), −160.61 (br, 4F; *meta*-F), −151.53 (t, $J = 17.6$ Hz, 4F; *para*-F), −137.47 (d, $J = 26.3$ Hz, 4F; *ortho*-F), −136.97 ppm (d, $J = 35.0$ Hz, 4F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1015 (4500), 795 (8400), 733 (8900), 577 (95000), 432 (3100), 338 nm (4600 $M^{-1}cm^{-1}$) nm; HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{62}H_{21}F_{20}N_6S_2$ ($[M+H]^+$): 1293.0944; found: 1293.0924 (100%); crystal data: $C_{62}H_{20}F_{20}N_6S_2$, $M_r = 1293$, monoclinic, space group $P2_1/n$ (No. 14), $a = 13.965(5)$, $b = 9.356(4)$, $c = 19.626(6)$ Å, $\beta = 103.92(1)°$, $V = 2488(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.725$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.061$ [$I > 2\sigma(I)$], $R_W = 0.188$ (all data), GOF = 1.174. Crystals were grown from $CHCl_3$/MeOH.

5,20-Bis(2-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin bis-Pd^{II} complex (12): Black solution, black solid, yield 53% ($Pd(OAc)_2$: 20.8 mg, 4 equiv); ^{1}H NMR ($CDCl_3$): $\delta = 2.68$ (d, $J = 4.8$ Hz, 2H; thienyl), 3.78 (d, $J = 4.8$ Hz, 2H; thienyl), 8.26 (d, $J = 4.8$ Hz, 2H; β-H), 8.44 (d, $J = 4.1$ Hz, 2H; β-H), 8.56 (d, $J = 4.4$ Hz, 2H; β-H), 9.05 (d, $J = 4.4$ Hz, 2H; β-H), 9.76 ppm (d, $J = 4.4$ Hz, 4H; β-H); ^{19}F NMR ($CDCl_3$): $\delta = -161.03$ (m, 2F; *meta*-F), −160.78 (m, 6F; *meta*-F), −150.64 (m, 8F; *para*-F), −137.02 (d, $J = 26.3$ Hz, 2F; *ortho*-F) −136.57 (m, 4F; *ortho*-F), −136.01 ppm (d, $J = 26.3$ Hz, 2F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1244 (7500), 911 (6500), 834 (7900), 736 (sh, 23000), 641 (35000), 552 (41000), 429 (38000), 367 nm (33000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{62}H_{16}F_{20}N_6S_2Pd_2$ ($[M]^+$): 1501.8649; found: 1501.8662 (100%); crystal data: $C_{62}H_{16}F_{20}N_6S_2Pd_2 \cdot 6\,CHCl_3$, $M_r = 2218$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.474(1)$, $b = 13.815(2)$, $c = 15.395(2)$ Å, $\alpha = 89.823(3)$, $\beta = 88.467(2)$, $\gamma = 88.467(2)°$, $V = 1901.6(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.937$ g cm^{-3}, $T = -183$ °C, $R_1 = 0.037$ [$I > 2\sigma(I)$], $R_W = 0.093$ (all data), GOF = 1.063. Crystals were grown from $CHCl_3$.

5,20-Bis(3-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin bis-Pd^{II} complex (13): Black solution, black solid, yield 62% ($Pd(OAc)_2$: 10.4 mg, 2 equiv); ^{1}H NMR ($CDCl_3$): $\delta = 0.66$ (d, $J = 5.0$ Hz, 2H; thienyl), 3.42 (d, $J = 5.0$ Hz, 2H; thienyl), 8.20 (d, $J = 4.6$ Hz, 2H; β-H), 8.49 (d, $J = 4.1$ Hz, 2H; β-H), 8.60 (d, $J = 4.6$ Hz, 2H; β-H), 9.05 (d, $J = 4.6$ Hz, 2H; β-H), 9.74 ppm (d, $J = 4.6$ Hz, 4H; β-H); ^{19}F NMR ($CDCl_3$): $\delta = -161.00$ (br, 2F; *meta*-F), −160.66 (br, 6F; *meta*-F), −150.47 (t, $J = 26.3$ Hz, 8F; *para*-F), −137.19 (d, $J = 26.3$ Hz, 2F; *ortho*-F) −136.58 (d, $J = 17.6$ Hz, 2F; *ortho*-F), −136.33 (d, $J = 26.3$ Hz, 2F; *ortho*-F), −136.08 ppm (d, $J = 26.3$ Hz, 2F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 1191 (7900), 898 (8000), 834 (7900), 630 (38000), 543 (39000), 470 (29000), 418 (34000), 390 nm (34000 $M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m/z* calcd for $C_{62}H_{19}F_{20}N_6S_2Pd_2$ ($[M+H]^+$): 1502.8727; found: 1502.8713 (100%); crystal data: $C_{62}H_{16}F_{20}N_6S_2Pd_2 \cdot 4\,CHCl_3 \cdot CCl_3 \cdot 8\,O$, $M_r = 2216$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.309(4)$, $b = 13.748(5)$, $c = 15.643(8)$ Å, $\alpha = 89.45(2)$, $\beta = 85.55(2)$, $\gamma = 73.05(1)°$, $V = 1909.0(1)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.937$ g cm^{-3}, $T = -150$ °C, $R_1 = 0.078$ [$I > 2\sigma(I)$], $R_W = 0.219$ (all data), GOF = 1.051. Crystals were grown from $CHCl_3$.

5,20-Bis(3-methyl-2-thienyl)-10,15,25,30-tetrakis(pentafluorophenyl)[28]-hexaphyrin (14): ^{1}H NMR ($CDCl_3$): $\delta = 2.01$ (s, 6H; methyl), 2.36 (br, 4H; innerβ-H), 4.02 (s, 2H; outer NH), 6.96 (d, $J = 5.0$ Hz, 2H; thienyl), 7.37 (d, $J = 5.0$ Hz, 2H; thienyl), 7.66 (d, $J = 4.1$ Hz, 2H; outer β-H), 7.73 (d, $J = 4.1$ Hz, 2H; outer β-H), 7.80 (d, $J = 4.6$ Hz, 2H; outer β-H),

7.94 ppm (s, 2H; outer β-H); ^{19}F NMR ($CDCl_3$): $\delta = -161.54$ (t, $J =$ 17.5 Hz, 4F; *meta*-F), −160.67 (s, 4F; *meta*-F), −153.27 (t, $J = 17.7$ Hz, 2F; *meta*-F), −151.81 (t, $J = 17.6$ Hz, 2F; *para*-F), −137.67 (d, $J = 17.6$ Hz, 4F; *ortho*-F), −137.13 ppm (d, $J = 26.3$ Hz, 4F; *ortho*-F); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 881 (4300), 775 (8200), 609 (120000), 444 (17000), 404 (22000), 314 nm ($16000\,M^{-1}cm^{-1}$); HR-ESI-TOF-Mass (positive-mode): *m*/*z* calcd for $C_{64}H_{27}F_{20}N_6S_2$ ($[M+H]^+$): 1323.1414; found: 1323.1437 (100%).

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[9] ^{1}H NMR data and X-ray crystal structures are supplied as Supporting Information.

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[12] Yield of **13** was only 26% yield for the metalation at room temperature, probably due to reactive nature of the thienyl 2-hydrogens that led to formation of undesirable products.

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