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[40]Nonaphyrin(1.1.1.1.1.1.1.1.1) and Its Heterometallic Complexes with Palladium–Carbon Bonds

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Abstract: *meso*-Pentafluorophenyl-substituted [40]nonaphyrin-(1.1.1.1.1.1.1.1.1) **3** has been prepared by using a stepwise ring-size-selective synthesis, and has been reduced with $NaBH_4$ to [42]nonaphyrin(1.1.1.1.1.1.1.1.1) **5**. Structurally, **3** is characterized by a figure-of-eight shape, consisting of a porphyrin-like tetrapyrrolic segment and a hexaphyrin-like hexapyrrolic segment, whereas **5** has been found to adopt a distorted nonplanar butterfly-like shape. In the mono-metal complexes **6** and **7**, a Zn^{II} or Cu^{II} ion is bound by the porphyrin-like tetrapyrrolic segment, maintaining the overall structure of **3**. Similarly to **3**, complexes **6** and **7** are interconvertible with the corresponding complexes **9** and **10** through two-electron reduction with $NaBH_4$ and oxidation with DDQ. The metal-free hexaphyrin-like segments of **6** and **7** have been shown to serve as a suitable platform for the complexation of two palladium ions, providing hetero-trinuclear metal complexes **11** (Zn^{II}–Pd^{II}–Pd^{II}) and **13** (Cu^{II}–Pd^{II}–Pd^{II}) in high yields, in which the Zn or Cu ion resides at the same porphyrin-like segment, and one Pd ion is bound in an NNCC fashion through double C−H bond activation while the other is bound in an NNC fashion with single C−H bond activation. Multimetal complexes **11**, **12**, and **13** exhibit small electrochemical HOMO–LUMO gaps (< 0.6 eV), despite their nonplanar conformations.

Keywords: conjugation · heterometallic complexes · HOMO–LUMO gap · macrocyclic ligands · porphyrinoids

Introduction

Expanded porphyrins incorporating more than four pyrrole units have been extensively studied because of their unique optical and electrochemical properties and complexation behaviors, which depend on ring size, ring connectivity, and the number of conjugated π electrons of the macrocycle.[1,2] One of the most fascinating functions of expanded porphyrins is that they can coordinate multiple metal ions within their large cavities, in contrast to porphyrins, which can accommodate most metal ions in only a 1:1 manner. Despite this coordination potential, only a limited number of homobis-metalated complexes of expanded porphyrins have hitherto been reported.[3] Recently, we have explored the synthesis of a series of *meso*-aryl-substituted expanded porphyrins on the basis of the reaction of pyrrole and pentafluorobenzaldehyde under modified Rothemund–Lindsey conditions (concentrations 67 mM each; $BF_3{\cdot}OEt_2$ in CH_2Cl_2, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)).[2] These *meso*-aryl-substituted expanded porphyrins can be regarded as real homologues of porphyrin, in view of the alternating arrangement of pyrroles and methine carbons. In the course of our studies on the metalation of these expanded porphyrins, we have elucidated their novel reactivities and properties, which are different for each expanded porphyrin, depending on their structural and electronic demands.[4] Representative examples are the oxidation-induced "rhodium-walk" of an Rh^I complex of N-fused pentaphyrin(1.1.1.1.1),[5] gable-type bis-Cu^{II}–hexaphyrins and their antiferromagnetic interactions,[6] a Cu^I-ion-induced double-pyrrolic rearrangement of a [26]hexaphyrin(1.1.1.1.1.1) to a doubly N-confused hexaphyrin,[7] aromatic and anti-aromatic switching of Au^{III}-metalated planar hexaphyrin(1.1.1.1.1.1),[8] sequential multiple N-fusion reactions of [32]heptaphyrin(1.1.1.1.1.1.1) and a boron complex of quadruply N-fused heptaphyrin,[9] a quantitative thermal splitting reaction of bis-Cu^{II} [36]octaphyrin(1.1.1.1.1.1.1.1) into two Cu^{II}–porphyrin molecules,[10] and partial hydrolytic cleavage of the pyrrole ring of perfluorinated [36]octaphyrin upon Cu^{II} ion

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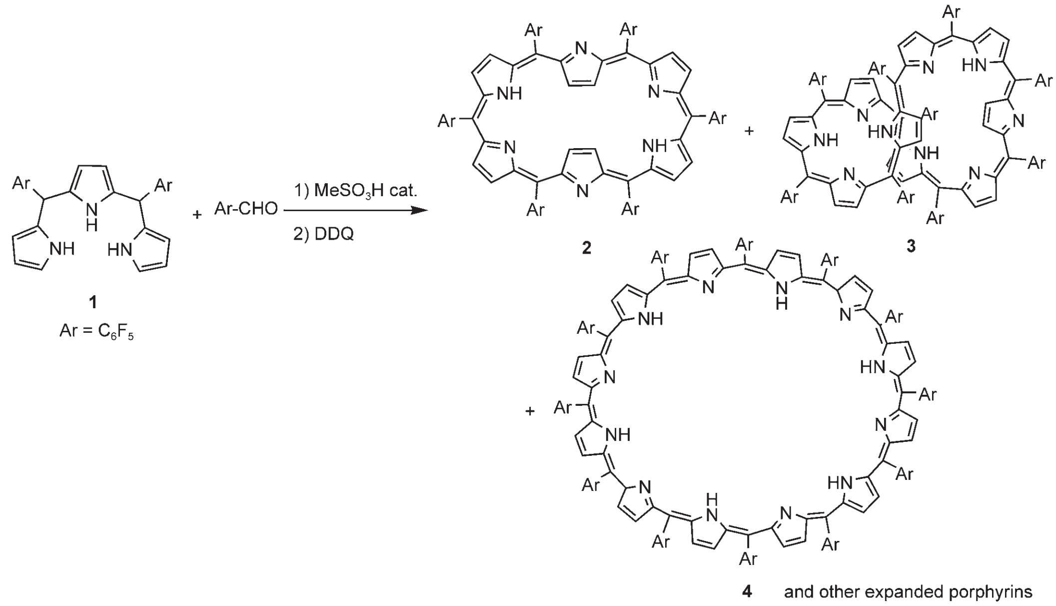
metalation.[11] Another attractive feature of the expanded porphyrins is that they can adopt more than two stable oxidation states, which are interconvertible through two-electron oxidation and reduction.[5,8] In addition, they are also of interest by virtue of their large two-photon absorption (TPA) cross sections.[12] Enhanced TPA properties are expected for larger expanded porphyrins, but their chemistry, especially their metal complexation behavior, has been only poorly studied, except for rare examples.[13] This is particularly the case for structures larger than octaphyrins, due in part to the increasing synthetic difficulty with increasing size. In the course of our investigations, we have elucidated the structure of the trifluoroacetic acid (TFA)-stabilized complex of [42]nonaphyrin(1.1.1.1.1.1.1.1.1) **5**,[2b] but the structure and properties of the corresponding free-base nonaphyrin were unknown. Thus, we have investigated the synthesis, redox behavior, and complexation chemistry of *meso*-pentafluorophenyl nonaphyrin(1.1.1.1.1.1.1.1.1), and we present our findings herein. In the metalation of [40]nonaphyrin **3**, positive heteroallosterism was employed to allow the effective formation of hetero-trinuclear metal complexes **11** and **13**.

Results and Discussion

Synthesis, structural characterization, and redox behavior of [40]nonaphyrin(1.1.1.1.1.1.1.1.1) (3): The nonaphyrin **3** was prepared in 15% yield along with hexaphyrin **2** (30%) and dodecaphyrin **4** (2%) by following our ring-size-selective synthetic protocol using tripyrrane **1** and pentafluorobenzaldehyde (22.2 mM each; at 0°C in CH_2Cl_2; 0.25 equiv methanesulfonic acid, and subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ))[2c] (Scheme 1). The reaction mixture was separated by using column chromatography on silica gel, eluting with a CH_2Cl_2/hexane mixture. A bright-green fraction containing **3** was collected and the product was recrystallized from CH_2Cl_2/hexane to give violet crystals. This method allowed us to prepare **3** on a large scale (ca. 280 mg) in one batch synthesis. High-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass measurement revealed the parent ion peak of **3** at m/z 2192.1369 ($[M+H]^+$; calcd for $C_{99}H_{23}F_{45}N_9$: 2192.1352). X-ray crystal structure analysis of **3** revealed a twisted asymmetric structure consisting of a helically arranged porphyrin-like tetrapyrrolic core (pyrroles **A**, **B**, **H**, and **I**) and a hexapyrrolic core (pyrroles **C**, **D**, **E**, **F**, **G**, and **H**), with two inverted pyrroles **E** and **H** (Figure 1). In accordance with this nonsymmetric structure, the ^1H NMR spectrum displayed eighteen peaks due to the β-CH protons in the range $\delta = 10.17$–5.67 ppm and four peaks due to the NH protons at $\delta = 16.41$, 14.44, 13.82, and 12.35 ppm. Reduction of **3** with $NaBH_4$ gave [42]nonaphyrin(1.1.1.1.1.1.1.1.1) **5**, the parent ion peak of which was observed in the HR-ESI-TOF mass spectrum at m/z 2194.1522 ($[M+H]^+$; calcd for $C_{99}H_{25}F_{45}N_9$: 2194.1509), in accordance with its formulation as [42]nonaphyrin. Solutions of **5** were dark green, but the product was purple in the solid state. It was found that the nonaphyrin **5** could be quantitatively oxidized to **3** by treatment with DDQ. The UV/Vis absorption spectrum of **5** showed a red-shift of approximately $\lambda = 30$ nm from that of **3** (Figure 2). The ^1H NMR spectrum of **5** featured six peaks due to NH protons at $\delta = 15.31$, 15.09, 14.88, 14.62, 13.65, and 13.10 ppm, and eighteen peaks due to β-CH protons in the range $\delta = 9.36$–5.26 ppm as the major peaks, thus indicating the non-aromaticity of **5**. In addition, sets of peaks attributable to the corresponding protons of the minor conformer could also be detected. X-ray diffraction analysis of **5** re-



Scheme 1. Ring-size-selective synthesis of nonaphyrin **3**.

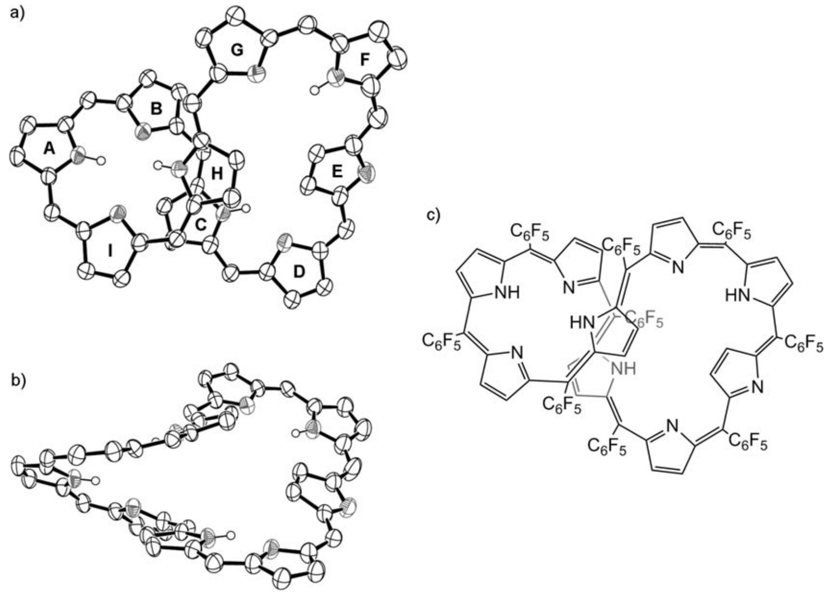


Figure 1. X-ray crystal structure of **3**: a) top view and b) side view. Peripheral substituents at the *meso*-position and hydrogen atoms at the β-positions have been omitted for clarity. c) Formal structure of **3**.

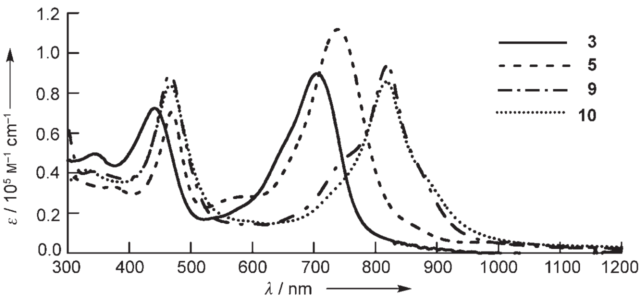


Figure 2. UV/Vis spectra of **3**, **5**, **9**, and **10** in CH_2Cl_2.

vealed a distorted asymmetric butterfly-like conformation (Figure 3), which is similar to that of the TFA-stabilized complex of [42]nonaphyrin(1.1.1.1.1.1.1.1.1).[2b] Intramolecular hydrogen bonding is observed between each adjacent amine NH and imine N of the pyrrole rings (**A**, **B**, and **C**; **D** and **E**; and **F**, **G**, and **H**).

Metalation behavior of 3: To investigate the coordination properties of nonaphyrin, we attempted metalations with Zn^{II} and Cu^{II} salts. Treatment of a solution of **3** in a 1:1 mixture of CH_2Cl_2 and methanol with an excess of $Zn(OAc)_2 \cdot 2H_2O$ in the presence of sodium acetate provided the mono-Zn^{II} complex **6** in 75 % yield, the parent ion peak of which was detected at *m*/*z* 2253.0460 ($[M]^-$; calcd for $C_{99}H_{20}F_{45}N_9Zn$: 2253.0420) in the HR-ESI-TOF mass spectrum. Even under more forcing conditions, no further zincation was observed. The solid-state structure of **6** has been determined by using X-ray diffraction analysis to have a twisted conformation similar to that of **3** (Figure 4a). The Zn^{II} ion is coordinated within the helically arranged porphyrin-like core consisting of the pyrroles **A**, **B**, **H**, and **I** with an average coordination bond length of 2.01 Å. The pyrroles **A**, **B**, and **I** are almost coplanar, with mean plane deviations of 0.18 Å, while pyrrole **H** is tilted with a dihedral angle of 52.2°. The metal-free portion of **6** forms a *meso*-aryl-substituted hexaphyrin-like rectangular segment consisting of the pyrroles **C**, **D**, **E**, **F**, **G**, and **H**. Of these, pyrroles **D**, **E**, **F**, and **G** are arranged in an almost coplanar manner, with a mean plane deviation of 0.15 Å. In accordance with the X-ray crystal structure, the ^{1}H NMR spectrum of **6** features eighteen signals due to the β-CH protons in the range $\delta = 12.99$–4.92 ppm and two signals due

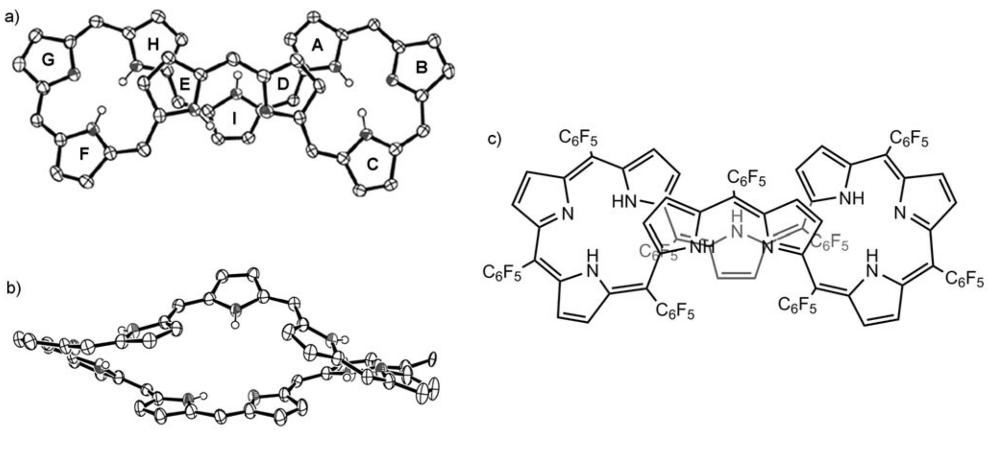


Figure 3. X-ray crystal structure of **5**: a) top view and b) side view. Peripheral substituents at the *meso*-position and hydrogen atoms at the β-positions have been omitted for clarity. c) Formal structure of **5**.

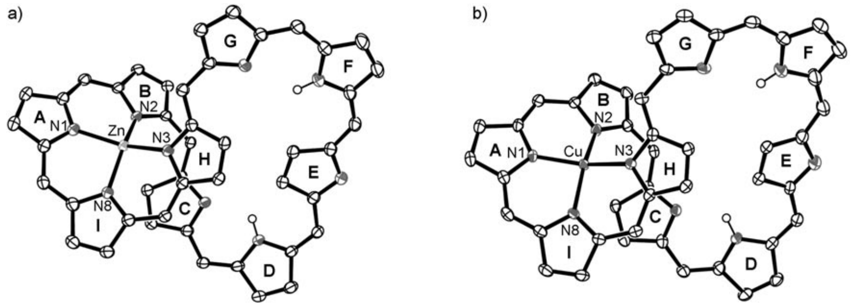


Figure 4. X-ray crystal structures of a) **6** and b) **7**. Peripheral substituents at the *meso*-position and hydrogen atoms at the β-positions have been omitted for clarity; selected bond lengths [Å] **6**: Zn−N1 2.014, Zn−N2 2.008, Zn−N3 2.024, Zn−N8 1.984; **7**: Cu−N1 1.966, Cu−N2 1.994, Cu−N3 1.996, Cu−N8 1.950.

to the NH protons at $\delta = 19.91$ and 17.98 ppm. The UV/Vis absorption spectrum of **6** exhibits absorption bands at $\lambda = 457$ and 741 nm, which are red-shifted relative to those of **3** (Figure 5).

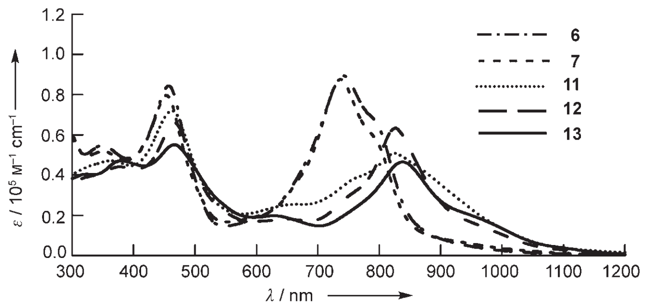
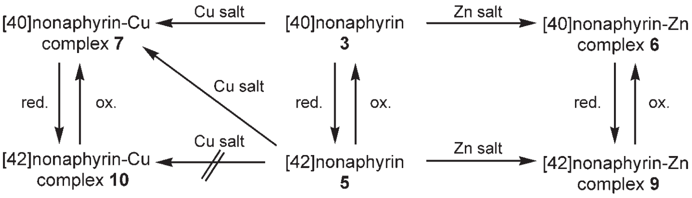


Figure 5. UV/Vis spectra of **6**, **7**, **11**, **12**, and **13** in CH_2Cl_2.

Under similar conditions, **3** was reacted with $Cu(OAc)_2$ to afford a mono-Cu^{II} complex (**7**) and a bis-Cu^{II} complex (**8**). The resulting mixture was separated by using column chromatography on silica gel, eluting with a CH_2Cl_2/hexane mixture. The first indigo-blue fraction contained **8** (12.5 mg, 27% yield) and the second yellow-green fraction contained **7** (15.7 mg, 35% yield). In the mass spectrum of complex **7**, the parent ion peak was seen at *m*/*z* 2252.0408 ($[M]^-$; calcd for $C_{99}H_{20}F_{45}N_9Cu$: 2252.0425). The structure of **7** has been explicitly determined by using X-ray analysis, which revealed a twisted conformation similar to those of **3** and **6** (Figure 4b). In **7**, the Cu^{II} ion is bound within the porphyrin-like core with an average coordination bond length of 1.97 Å, which is similar to that in related porphyrins (1.99 Å in the case of CuTFPP).[14] In the porphyrin-like core, pyrroles **A**, **B**, and **I** are almost coplanar with a mean plane deviation of 0.16 Å, while pyrrole **H** is tilted with a dihedral angle of 44.3°. The absorption spectrum of **7** features bands at $\lambda = 453$ and 737 nm (Figure 5). In the mass spectrum of complex **8**, the parent ion peak was observed at *m*/*z* 2311.9511 ($[M{-}H]^-$; calcd for $C_{99}H_{17}F_{45}N_9Cu_2$: 2311.9486), which indicates the coordination of two Cu ions. Structural characterization of **8**, however, has been hampered by its instability. Upon standing in solution exposed to air, **8** was converted to its oxygenated product, as judged from the mass spectrum.

Reduction of mono-metal complexes 6 and 7: Reductions of the mono-metal complexes **6** and **7** were also examined. Similarly to the free base **3**, complexes **6** and **7** were smoothly reduced with $NaBH_4$ to the mono-Zn^{II} complex **9** and the mono-Cu^{II} complex **10** without demetalation. These two complexes can be formulated as [42]nonaphyrins. Low-energy absorption bands were observed at $\lambda = 819$ and 818 nm for **9** and **10**, respectively. Although the X-ray crystal structures of **9** and **10** have yet to be determined, these complexes may be considered to adopt similar conformations as in the case of **5**, in view of the similarity of their absorption spectra. Complexes **9** and **10** could be quantitatively oxidized back to **6** and **7** by treating them with DDQ or MnO_2. Metalation of **5** with Zn^{II} ions gave complex **9** in 78% yield, whereas metalation of **5** with Cu^{II} ions afforded the complexes **7** and **8** in yields of just 42% and 25%, respectively, probably as a result of instantaneous oxidation of **5** to **3** by Cu^{II} ions (Scheme 2).



Scheme 2. Redox behavior of nonaphyrins.

Trinuclear metal complexes: Since the mono-metalated complexes **6** and **7** possess planar hexaphyrin-like moieties that may accommodate additional metal ions, further metalations were attempted with various metal salts. After many attempts, we found that the metalation of **6** with $Pd(OAc)_2$ in a mixture of CH_2Cl_2 and MeOH (1:10) in the presence of NaOAc at room temperature quantitatively afforded the brown trinuclear (Zn–Pd–Pd) complex **11**. In the mass spectrum of **11**, the parent ion peak was seen at *m*/*z* 2459.8140 ($[M{-}H]^-$; calcd for $C_{99}H_{15}N_9F_{45}ZnPd_2$: 2459.8129). Preliminary X-ray analysis of **11** indicated a distorted nonplanar structure, in which the Zn^{II} ion resides within the porphyrin-like tetrapyrrolic core and the two Pd^{II} ions are effectively accommodated within the remaining hexaphyrin-like segment. In the ^{1}H NMR spectrum of **11**, fourteen signals due to β-protons appear in the range $\delta = 10.60$–3.46 ppm; proton **H**(1) gives rise to a singlet at $\delta = 4.63$ ppm (for the designation of **H**(1), cf. the similar proton in Figure 6a) and the signal of the outer NH proton is seen at $\delta = 5.89$ ppm.

Under similar conditions, in the absence of sodium acetate, metalation of **7** with $Pd(OAc)_2$ provided the $CuPd_1$ complex **12** and the $CuPd_2$ complex **13** in yields of 16% and 46%, respectively. More forcing metalation conditions (reflux in the presence of sodium acetate) led to quantitative conversion to **13**, suggesting the stepwise formation of **12** and **13** from **7**. The parent ion peaks were observed in the HR-ESI-TOF mass spectra at *m*/*z* 2354.9250 ($[M-H]^-$; calcd for $C_{99}H_{17}N_9F_{45}CuPd$: 2354.9253) for **12** and at *m*/*z* 2458.8181 ($[M-H]^-$; calcd for $C_{99}H_{15}N_9F_{45}CuPd_2$: 2458.8138) for **13**. While only a preliminary crystal structure was obtained for **12** (Supporting Information), the structure of **13** has been determined by using X-ray diffraction analysis (Figure 6). In the latter, the Cu ion resides in the familiar porphyrin-like core consisting of pyrroles **A**, **B**, **H**, and **I**, the Pd1 ion is bound by C23, N6, N7, and C37 in an NNCC fashion analogous to doubly N-confused porphyrin-like coordination,[15] and the Pd2 ion is bound by N3, N4, and C22. Interestingly, the distance between Pd2 and C38 is 2.23 Å, which is distinctly longer than a normal C−Pd bond length, but is exactly what one would expect for an agostic interaction, thus suggesting an agostic interaction between Pd2 and the C−H bond of pyrrole **H**.[16] As a consequence of the coordination of the two palladium ions, the tetrapyrrolic segment consisting of pyrroles **D**, **E**, **F**, and **G** becomes more coplanar in **13**, with a mean plane deviation of 0.12 Å, while pyrrole **H** is tilted at a dihedral angle of 33.6°. The absorption spectra of **11**, **12**, and **13** are similar to one another, and are considerably broader than those of **6** and **7** (Figure 5).

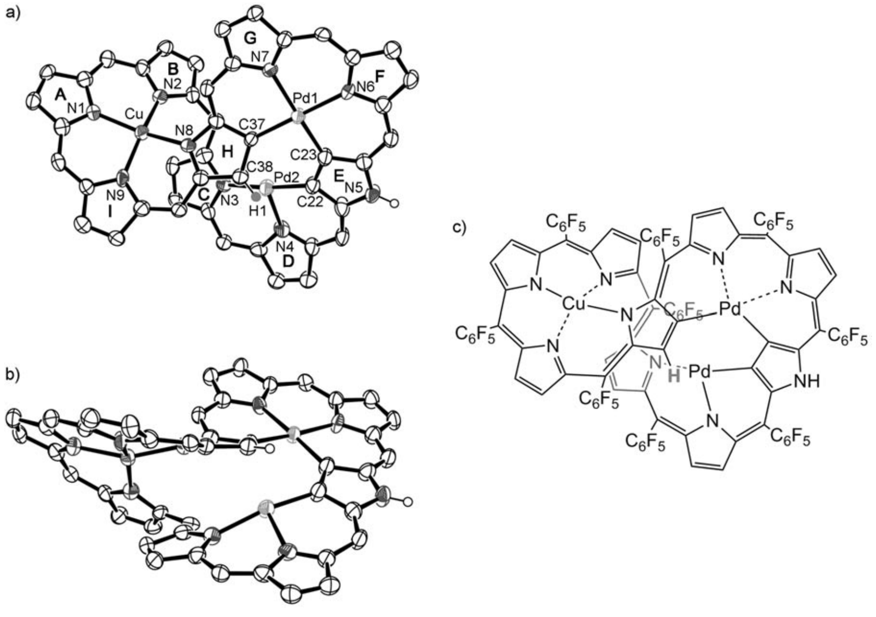


Figure 6. X-ray crystal structures of **13**; a) top view and b) side view. Peripheral substituents at the *meso*-position and hydrogen atoms at the β-positions (except H1) have been omitted for clarity; selected bond lengths [Å]: Cu−N1 1.975, Cu−N2 2.014, Cu−N8 2.011, Cu−N9 1.951, Pd1−N6 2.075, Pd1−N7 2.058, Pd1−C23 1.955, Pd1−C37 1.970, Pd2−N3 2.071, Pd2−N4 2.038, Pd2−C22 1.932, Pd2⋯C38 2.226. c) Formal structure of **13**.

It is important to note that the quantitative formation of **11** or **13** is only possible by using **6** or **7** as starting substrates. Attempted metalations of **3** in the presence of both Cu^{II} and Pd^{II} ions or with Pd^{II} ions alone under various conditions gave very complicated intractable mixtures, underscoring the importance of the pre-coordination of the Cu^{II} or Zn^{II} ion for the clean formation of **11** and **13**. It is probable that the pre-coordination fixes the porphyrin-like tetrapyrrolic segment, thereby imposing a somewhat constrained structure on the hemi-hexaphyrin-like segment, which facilitates the subsequent mono- and bis-palladations. As has recently been explored, expanded porphyrins represent a class of promising multi-metal ligands, but, with increasing size of the macrocycles, their metalation behavior becomes ever more difficult to control, mainly due to the increasing diversity of possible conformations. In this respect, our stepwise metalation protocol based on positive hetero- or homoallosterism may be useful for controlled metalation.

Cyclic voltammograms of 3, 6, 7, 11, 12, and 13: Additional attractive attributes of the multinuclear complexes **11**, **12**, and **13** are their small electrochemical HOMO–LUMO gaps (Figure 7). Cyclic voltammetry (Pt working electrode, scan rate $0.1\ V\,s^{-1}$, in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate, versus ferrocene/ferrocenium ion) has revealed that **3** undergoes a reversible oxidation at 0.35 V and two reversible reductions at −0.52 and −0.77 V, and that complexes **6** and **7** display two reversible oxidations at 0.22 and 0.53 V and at 0.25 and 0.57 V, respectively, and two reversible reductions at −0.45 and −0.75 V and at −0.48 and −0.80 V, respectively. Thus, the electrochemical HOMO–LUMO gaps are rather small, at 0.87, 0.67, and 0.73 V for **3**, **6**, and **7**, respectively. Curiously, the trinuclear complexes **11** and **13** exhibit two reversible oxidations at 0.17 and 0.54 V and at 0.16 and 0.53 V, respectively, and two reversible reductions at −0.42 and −0.79 V and at −0.42 and −0.80 V, respectively. The electrochemical HOMO–LUMO gaps for **11** and **13** are thus 0.59 and 0.58 V, which are distinctly smaller than those of related octaphyrins[3d] and comparable to that (0.60 V) of cyclo[8]pyrrole,[17] which, to the best of our knowledge, has been the smallest gap hitherto reported for a metal complex of an expanded porphyrin.

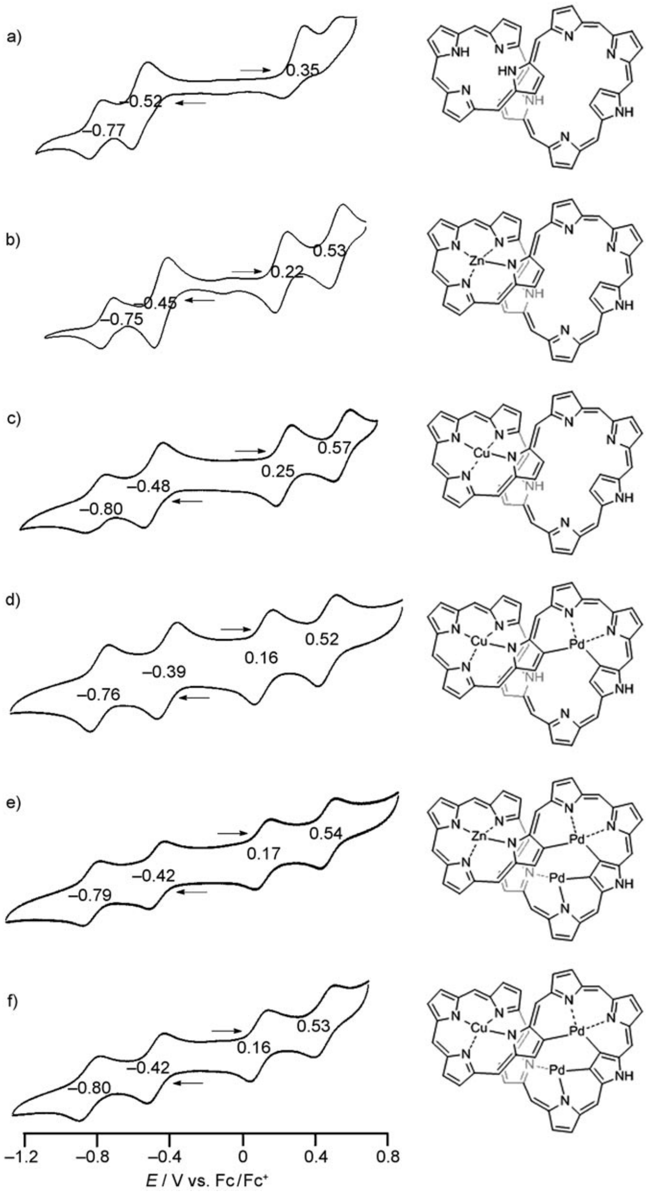


Figure 7. Cyclic voltammograms of a) **3**, b) **6**, c) **7**, d) **12**, e) **11**, and f) **13** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ obtained at a Pt working electrode (scan rate 0.1 $V s^{-1}$).

The small HOMO–LUMO gap of cyclo[8]pyrrole has been attributed to its large 30π electronic system, which is almost planar. Interestingly, the electrochemical HOMO–LUMO gap of complex **12** is even smaller, amounting to just 0.55 V. The very small HOMO–LUMO gaps of these complexes are remarkable, considering their distorted nonplanar figure-of-eight conformations.

Conclusion

In summary, the [40]nonaphyrin(1.1.1.1.1.1.1.1.1) **3** has been prepared by using a stepwise ring-size-selective synthesis and has been reduced with $NaBH_4$ to the [42]nonaphyrin(1.1.1.1.1.1.1.1.1) **5**. The structure of **3** has been identified as having a figure-of-eight shape consisting of a porphyrin-like tetrapyrrolic segment and a hexaphyrin-like hexapyrrolic segment, while the structure of **5** has been characterized as having a distorted butterfly-like shape. The nonaphyrin **3** has been converted into the mono-Zn^{II} complex **6** and the mono-Cu^{II} complex **7**, in which the respective metal ions are bound within the porphyrin-like core. Complexes **6** and **7** have been shown to serve as suitable precursors for the assembly of the trinuclear metal complexes **11** (Zn^{II}–Pd^{II}–Pd^{II}) and **13** (Cu^{II}–Pd^{II}–Pd^{II}). Complex **13** has been found to adopt a distorted nonplanar structure, in which the Pd1 ion is bound in an NNCC fashion as in a doubly N-confused porphyrin and the Pd2 ion is bound in an NNC fashion with an agostic interaction with the bridgehead pyrrole **H**. Curiously, the metal complexes **6**, **7**, **11**, **12**, and **13** display small electrochemical HOMO–LUMO gaps despite their distorted nonplanar structures.

Experimental Section

General procedures: All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by distillation over CaH_2. ^1H and ^{19}F NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating at 600.17 MHz for ^1H and at 564.73 MHz for ^{19}F) using the residual solvent signal as an internal reference for ^1H ($\delta = 7.260$ ppm for $CHCl_3$ in $CDCl_3$) and hexafluorobenzene as an external reference for ^{19}F ($\delta = -162.9$ ppm). Spectroscopic grade CH_2Cl_2 was used as solvent for all UV/Vis spectroscopic studies. UV/Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Mass spectra were recorded on either a JEOL HX-110 spectrometer, operating in the positive FAB ionization mode with an accelerating voltage of 10 kV and 3-nitrobenzyl alcohol as the matrix; a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer operating in the positive MALDI ionization mode; or a BRUKER microTOF spectrometer operating in positive- and negative-ion modes with acetonitrile as solvent. Preparative separations were performed by using flash column chromatography on silica gel (Merck Kieselgel 60H Art. 7736) or by using gravity column chromatography on silica gel (Wako gel C-200, C-300, and C-400) or alumina (Sumitomo Chemical KC-1525).

Crystallographic data collections and structure refinement: Crystallographic data for compounds **3**, **5**, and **13** were collected at −150 °C on a Rigaku RAXIS-RAPID apparatus using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Data for compounds **6** and **7** were collected at $T = -183$ °C on a Bruker SMART APEX apparatus, also using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Details of the crystal structure determinations are listed in Table 1. The structures were solved by using direct methods (SIR-97[18] or SHELXS-97[19]) and refined by applying Rigaku CrystalStructure software or by full-matrix least-squares techniques (SHELXL-97).[19] CCDC-622794 (**3**), -620155 (**5**), -620156 (**6**), -620157 (**7**), and -620158 (**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.au.uk/data_request/cif.

***meso*-Pentafluorophenyl-substituted [40]nonaphyrin (3)**: A solution of 5,10-bis(pentafluorophenyl)tripyrrane (**1**) (1.39 g, 2.5 mmol) and pentafluorobenzaldehyde (0.3 mL, 2.5 mmol) in CH_2Cl_2 (110 mL) (22.2 mM) was stirred for 2 h under N_2 with protection from light at 0 °C. Thereafter, 2.5 M methanesulfonic acid (MSA) in CH_2Cl_2 (125 μL, 0.125 equiv) was added to the solution. After a further 2 h, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.83 g, 12.5 mmol, 5 equiv) was added, and the resulting solution was stirred overnight at room temperature. The reaction

Table 1. Crystal data and structure refinement of **3**, **5**, **6**, **7**, and **13**.

	3	**5**	**6**	**7**	**13**
formula	$C_{117}H_{46}F_{45}N_9$	$C_{100}H_{26}Cl_2F_{45}N_9O$	$C_{99}H_{20}F_{45}N_9OZn$	$C_{111}H_{34}CuF_{45}N_9O_2$	$C_{111}H_{23}CuF_{45}N_9Pd_2$
M_r	2426.62	2298.09	2271.61	2444.01	2613.72
T [K]	123	123	90	90	123
crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	triclinic
space group	*Pbca*(no. 61)	*P*1 (no. 2)	$P2_1/c$ (no. 14)	*Pbca* (no. 61)	*P*1 (no. 2)
a [Å]	27.235(5)	15.059(4)	14.5361(12)	27.128(11)	13.731(3)
b [Å]	20.325(3)	15.745(4)	22.0518(18)	20.317(8)	17.300(5)
c [Å]	38.101(5)	19.371(6)	26.669(2)	37.640(15)	22.157(7)
α [°]	90	86.836(11)	90	90	72.651(10)
β [°]	90	79.811(10)	95.5350(10)	90	85.300(11)
γ [°]	90	80.680(11)	90	90	78.057(9)
V [Å^3]	21 090(6)	4459(2)	8508.8(12)	20 746(14)	4914(2)
Z	8	2	4	8	2
ρ_{calcd} [g cm^{-3}]	1.528	1.712	1.773	1.565	1.766
μ [mm^{-1}]	0.147	0.227	0.448	0.348	0.720
F(000)	9704	2275	4480	9704	2556
crystal size [mm^3]	0.60 × 0.20 × 0.05	0.50 × 0.15 × 0.10	0.45 × 0.35 × 0.20	0.45 × 0.20 × 0.10	0.20 × 0.10 × 0.05
$2\theta_{max}$ [°]	56.2	55.2	56.4	54.7	50.0
observed reflns	18 299	20 366	20 179	24 185	17 024
total reflns	124 048	45 507	98 955	123 426	38 249
parameters	1607	1515	1415	1545	1469
absorpn correction	none	none	none	empirical	none
R_1 [$I > 2\sigma(I)$]	0.0883	0.0762	0.609	0.0742	0.0832
wR_2 (all data)	0.2805	0.2412	0.1792	0.2398	0.2677
GoF	1.017	1.024	1.024	0.971	1.030

was ultimately quenched by passing the mixture through a column of alumina. The eluate was concentrated and then separated by using column chromatography on silica gel (Wako gel C-400) to give [26]hexaphyrin(1.1.1.1.1.1) **2** (510 mg, 0.35 mmol, 30 %), [40]nonaphyrin(1.1.1.1.1.1.1.1.1) **3** (280 mg, 0.13 mmol, 15 %), and dodecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1) **4** (35 mg, 12 μmol, 2 %). At this scale of reaction, we also observed the formation of porphyrin and other expanded porphyrins, including pentaphyrin, heptaphyrin, octaphyrin, decaphyrin, and undecaphyrin, by means of TLC and MALDI TOF-MS analyses. Crystals of **3** suitable for X-ray crystallographic analysis were grown by means of vapor diffusion of heptane into a solution of the compound in CH_2Cl_2. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 16.41 (s, 1 H; NH), 14.44 (s, 1 H; NH), 13.82 (s, 1 H; NH), 12.35 (s, 1 H; NH), 10.17 (d, J = 4.1 Hz, 1 H; β-H), 9.81 (d, J = 4.0 Hz, 1 H; β-H), 9.76 (d, J = 4.1 Hz, 1 H; β-H), 7.99 (d, J = 4.7 Hz, 1 H; β-H), 7.95 (d, J = 4.6 Hz, 1 H; β-H), 6.78 (d, J = 4.6 Hz, 1 H; β-H), 6.77 (s, 1 H; β-H), 6.73 (s, 1 H; β-H), 6.65 (s, 1 H; β-H), 6.53 (d, J = 4.1 Hz, 1 H; β-H), 6.40 (s, 1 H; β-H), 6.24 (d, J = 4.1 Hz, 1 H; β-H), 6.19 (d, J = 4.2 Hz, 1 H; β-H), 6.15 (d, J = 4.0 Hz, 1 H; β-H), 6.08 (d, J = 4.1 Hz, 1 H; β-H), 6.05 (d, J = 4.6 Hz, 1 H; β-H), 5.92 (d, J = 3.7 Hz, 1 H; β-H), 5.67 ppm (d, J = 3.8 Hz, 1 H; β-H); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = −133.6 (d, J = 20.7 Hz, 1 F; *o*-Ar), −134.1 (d, J = 19.0 Hz, 1 F; *o*-Ar), −134.5 (d, J = 20.7 Hz, 1 F; *o*-Ar), −135.0 (m, 1 F; *o*-Ar), −135.5 (m, 2 F; *o*-Ar), −136.5 (m, 3 F; *o*-Ar), −137.9 (d, J = 20.7 Hz, 1 F; *o*-Ar), −138.0 (d, J = 17.3 Hz, 1 F; *o*-Ar), −138.3 (m, 1 F; *o*-Ar), −138.9 (m, 1 F; *o*-Ar), −139.2 (d, J = 22.4 Hz, 1 F; *o*-Ar), −139.6 (m, 2 F; *o*-Ar), −139.9 (m, 1 F; *o*-Ar), −140.2 (m, 1 F; *o*-Ar), −151.4 (q, J = 20.7 Hz, 1 F; *p*-Ar), −151.6 (q, J = 22.4 Hz, 1 F; *p*-Ar), −152.1 (m, 2 F; *p*-Ar), −152.7 (m, 3 F; *p*-Ar), −154.3 (t, J = 20.7 Hz, 1 F; *p*-Ar), −154.9 (t, J = 20.7 Hz, 1 F; *p*-Ar), −158.0 (m, 1 F; *m*-Ar), −159.1 (m, 1 F; *m*-Ar), −160.6 (t, J = 19.0 Hz, 1 F; *m*-Ar), −160.8 (t, J = 20.7 Hz, 1 F; *m*-Ar), −161.2 (m, 7 F; *m*-Ar), −161.6 (t, J = 20.7 Hz, 1 F; *m*-Ar), −161.8 (t, J = 20.7 Hz, 1 F; *m*-Ar), −162.0 (q, J = 22.4 Hz, 1 F; *m*-Ar), −163.3 (t, J = 18.9 Hz, 1 F; *m*-Ar), −163.5 (t, J = 20.7 Hz, 1 F; *m*-Ar), −164.6 (t, J = 20.7 Hz, 1 F; *m*-Ar), −165.1 ppm (t, J = 21.5 Hz, 1 F; *m*-Ar); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 342 (50 000), 442 (72 000), 705 nm (90 000); HR-ESI-TOF-MS: *m*/*z*: calcd for $C_{99}H_{23}F_{45}N_9$: 2192.1352; found: 2192.1369 [M+H]$^+$.

***meso*-Pentafluorophenyl-substituted [42]nonaphyrin (5)**: $NaBH_4$ (7.6 mg, 0.2 mmol, 10 equiv) was carefully added in small portions to a stirred solution of **3** (43.8 mg, 20 μmol) in a 1:1 mixture of CH_2Cl_2 and methanol and the resulting mixture was stirred for 30 min. The reaction was then quenched by the addition of water. The organic layer was washed with brine and dried over Na_2SO_4. Removal of the solvent gave **5** almost quantitatively. Crystals of **5** suitable for X-ray crystallographic analysis were grown by means of vapor diffusion of hexane into a solution of the compound in CH_2Cl_2. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) (major peaks): δ = 15.31 (s, 1 H; NH), 15.09 (br s, 1 H; NH), 14.88 (s, 1 H; NH), 14.62 (br s, 1 H; NH), 13.65 (s, 1 H; NH), 13.10 (s, 1 H; NH), 9.36 (d, J = 2.9 Hz, 1 H; β-H), 7.54 (d, J = 4.5 Hz, 1 H; β-H), 7.47 (d, J = 3.8 Hz, 1 H; β-H), 7.37 (s, 1 H; β-H), 7.05 (s, 1 H; β-H), 6.91 (d, J = 4.4 Hz, 1 H; β-H), 6.54 (s, 2 H; β-H), 6.35 (d, J = 4.8 Hz, 1 H; β-H), 6.25 (d, J = 3.5 Hz, 1 H; β-H), 6.10 (d, J = 3.8 Hz, 1 H; β-H), 6.03 (d, J = 4.2 Hz, 1 H; β-H), 6.01 (d, J = 4.1 Hz, 1 H; β-H), 5.80 (s, 1 H; β-H), 5.72 (d, J = 3.8 Hz, 1 H; β-H), 5.69 (d, J = 3.2 Hz, 1 H; β-H), 5.56 (d, J = 2.9 Hz, 1 H; β-H), 5.26 ppm (s, 1 H; β-H); ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = −131.5 (dd, J = 56.9 Hz, J = 17.3 Hz, 1 F; *o*-Ar), −134.1 (d, J = 22.4 Hz, 1 F; *o*-Ar), −134.3 (m, 2 F; *o*-Ar), −135.1 (dd, J = 55.2 Hz, J = 13.8 Hz, 1 F; *o*-Ar), −135.8 (d, J = 20.7 Hz, 1 F; *o*-Ar), −136.6 (m, 1 F; *o*-Ar), −137.1 (d, J = 22.4 Hz, 1 F; *o*-Ar), −137.9 (d, J = 20.7 Hz, 1 F; *o*-Ar), −138.2 (m, 4 F; *o*-Ar), −138.6 (m, 4 F; *o*-Ar), −140.5 (m, 1 F; *o*-Ar), −147.7 (t, J = 20.7 Hz, 1 F; *p*-Ar), −149.9 (m, 1 F; *p*-Ar), −151.7 (t, J = 21.5 Hz, 1 F; *p*-Ar), −151.9 (m, 1 F; *p*-Ar), −152.1 (m, 1 F; *p*-Ar), −152.5 (m, 1 F; *p*-Ar), −152.7 (m, 1 F; *p*-Ar), −153.0 (m, 2 F; *p*-Ar), −156.0 (m, 1 F; *m*-Ar), −157.1 (t, J = 19.8 Hz, 1 F; *m*-Ar), −158.1 (m, 2 F; *m*-Ar), −158.9 (m, 1 F; *m*-Ar), −160.1 (m, 1 F; *m*-Ar), −160.3 (m, 1 F; *m*-Ar), −160.5 (m, 3 F; *m*-Ar), −160.8 (m, 4 F; *m*-Ar), −161.0 ppm (m, 4 F; *m*-Ar) (beside these signals, sets of minor peaks were observed, suggesting the presence of minor conformers of **5** in solution); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 469 (70 000), 739 nm (111 000); HR-ESI-TOF-MS: *m*/*z*: calcd for $C_{99}H_{25}F_{45}N_9$: 2194.1509; found: 2194.1522 [M+H]$^+$.

Zn^{II} complex of [40]nonaphyrin (6): A solution of **3** (43.8 mg, 20 μmol) and NaOAc (3.3 mg, 40 μmol, 2 equiv) in a 1:1 mixture of CH_2Cl_2 and methanol was stirred under N_2 at room temperature. $Zn(OAc)_2 \cdot 2H_2O$ (43.9 mg, 0.2 mmol, 10 equiv) was then added, and after 15–30 min the reaction mixture was washed with brine, dried with Na_2SO_4, and the solvent was removed. The residual mixture was separated by using column chromatography on silica gel (Wako gel C-400) to give complex **6** (33.6 mg, 15 μmol, 75 %). Crystals of **6** suitable for X-ray crystallographic analysis were grown by means of vapor diffusion of hexane into a solution of the compound in CH$_2$Cl$_2$. ^{1}H NMR (600 MHz, CDCl$_3$, 298 K): δ = 19.91 (s, 1H; NH), 17.98 (s, 1H; NH), 12.99 (s, 1H; β-H), 12.47 (s, 1H; β-H), 12.32 (s, 1H; β-H), 9.60 (s, 1H; β-H), 7.52 (s, 1H; β-H), 7.16 (s, 1H; β-H), 7.02 (s, 1H; β-H), 6.46 (s, 1H; β-H), 6.41 (s, 1H; β-H), 6.26 (s, 2H; β-H), 6.04 (s, 1H; β-H), 5.70 (s, 1H; β-H), 5.63 (s, 1H; β-H), 5.39 (s, 1H; β-H), 5.34 (s, 1H; β-H), 5.12 (s, 1H; β-H), 4.92 ppm (s, 1H; β-H); ^{19}F NMR (565 MHz, CDCl$_3$, 298 K): δ = −127.5 (brs, 1F; *o*-Ar), −128.6 (m, 1F; *o*-Ar), −130.8 (d, *J* = 23.3 Hz, 1F; *o*-Ar), −132.0 (d, *J* = 21.6 Hz, 1F; *o*-Ar), −132.6 (d, *J* = 19.0 Hz, 1F; *o*-Ar), −134.2 (m, 1F; *o*-Ar), −134.7 (d, *J* = 23.3 Hz, 1F; *o*-Ar), −134.9 (d, *J* = 21.1 Hz, 1F; *o*-Ar), −136.2 (d, *J* = 20.7 Hz, 1F; *o*-Ar), −136.4 (d, *J* = 17.3 Hz, 2F; *o*-Ar), −137.0 (m, 3F; *o*-Ar), −137.3 (d, *J* = 21.6 Hz, 1F; *o*-Ar), −138.0 (m, 1F; *o*-Ar), −139.5 (m, 2F; *o*-Ar), −148.8 (m, 1F; *p*-Ar), −149.5 (t, *J* = 21.6 Hz, 1F; *p*-Ar), −150.4 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −151.3 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −151.6 (dd, *J* = 55.0 Hz, *J* = 20.7 Hz, 2F; *p*-Ar), −152.2 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −153.4 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −153.6 (t, *J* = 21.2 Hz, 1F; *p*-Ar), −156.1 (m, 1F; *m*-Ar), −156.5 (m, 1F; *m*-Ar), −159.3 (t, *J* = 23.3 Hz, 1F; *m*-Ar), −159.5 (m, 2F; *m*-Ar), −159.8 (m, 3F; *m*-Ar), −160.0 (m, 1F; *m*-Ar), −160.1 (m, 2F; *m*-Ar), −160.3 (t, *J* = 22.0 Hz, 1F; *m*-Ar), −160.4 (t, *J* = 21.6 Hz, 1F; *m*-Ar), −160.5 (t, *J* = 21.6 Hz, 1F; *m*-Ar), −162.3 (m, 2F; *m*-Ar), −163.6 (t, *J* = 21.6 Hz, 1F; *m*-Ar), −164.1 ppm (t, *J* = 22.0 Hz, 1F; *m*-Ar); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 350 (55000), 457 (84000), 741 nm (89000); HR-ESI-TOF-MS: *m*/*z*: calcd for C$_{99}$H$_{20}$F$_{45}$N$_9$Zn: 2253.0420; found: 2253.0460 [*M*]$^-$.

Cu^{II} complexes of [40]nonaphyrin (7) and (8): A solution of **3** (43.8 mg, 20 μmol) and NaOAc (3.3 mg, 40 μmol) in a 1:1 mixture of CH$_2$Cl$_2$ and methanol was stirred under N$_2$ at room temperature. Cu(OAc)$_2$ (24.5 mg, 0.2 mmol, 10 equiv) was then added, and after 15–30 min the reaction mixture was washed with brine, dried with Na$_2$SO$_4$, and the solvent was removed. The residual mixture was separated by using column chromatography on silica gel (Wako gel C-400) to give mono-Cu^{II} complex **7** (15.7 mg, 6.9 μmol, 35%) and bis-Cu^{II} complex **8** (12.5 mg, 5.4 μmol, 27%). Crystals of **7** suitable for X-ray crystallographic analysis were grown by means of vapor diffusion of hexane into a solution of the compound in CH$_2$Cl$_2$.

Mono-Cu^{II} complex of [40]nonaphyrin (7): UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 351 (52000), 453 (80000), 737 nm (87000); HR-ESI-TOF-MS: *m*/*z*: calcd for C$_{99}$H$_{20}$F$_{45}$N$_9$Cu: 2252.0425; found: 2252.0408 [*M*]$^-$.

Bis-Cu^{II} complex of [40]nonaphyrin (8): UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 348 (84000), 594 (90000), 780 nm (94000); HR-ESI-TOF-MS: *m*/*z*: calcd for C$_{99}$H$_{17}$F$_{45}$N$_9$Cu$_2$: 2311.9486; found: 2311.9511 [*M*−H]$^-$.

Zn^{II} complex of [42]nonaphyrin (9): NaBH$_4$ (3.8 mg, 0.1 mmol, 10 equiv) was carefully added in small portions to a stirred solution of **6** (22.5 mg, 10 μmol) in a 1:1 mixture of CH$_2$Cl$_2$ and methanol and stirring was continued for a further 30 min. The reaction was then quenched with water and the mixture was washed with brine and dried over Na$_2$SO$_4$. Removal of the solvent left a quantitative yield of the mono-Zn complex of [42]nonaphyrin **9**. Alternatively, treatment of **5** with Zn(OAc)$_2$·2H$_2$O gave the same product in 78% yield. ^{1}H NMR (600 MHz, CDCl$_3$, 298 K): δ = 9.94 (s, 1H; NH), 8.86 (d, *J* = 4.8 Hz, 1H; β-H), 8.59 (s, 1H; NH), 7.47 (d, *J* = 4.4 Hz, 1H; β-H), 7.38 (d, *J* = 4.9 Hz, 1H; β-H), 7.21 (d, *J* = 4.3 Hz, 1H; β-H), 7.09 (d, *J* = 4.5 Hz, 1H; β-H), 7.06 (s, 1H; β-H), 6.92 (s, 1H; β-H), 6.67 (s, 1H; β-H), 6.61 (s, 1H; β-H), 6.43 (s, 1H; β-H), 6.27 (d, *J* = 4.8 Hz, 1H; β-H), 6.00 (d, *J* = 4.4 Hz, 1H; β-H), 5.62 (d, *J* = 4.2 Hz, 1H; β-H), 4.76 (d, *J* = 4.1 Hz, 1H; β-H), 4.40 (s, 1H; β-H), 4.03 (d, *J* = 4.1 Hz, 1H; β-H), 3.41 (s, 1H; NH), 3.15 (d, *J* = 4.8 Hz, 1H; β-H), 3.10 (d, *J* = 4.8 Hz, 1H; β-H), 2.69 ppm (s, 1H; NH); ^{19}F NMR (565 MHz, CDCl$_3$, 298 K): δ = −131.3 (dd, *J* = 65.6 Hz, *J* = 23.3 Hz, 1F; *o*-Ar), −131.9 (d, *J* = 20.7 Hz, 1F; *o*-Ar), −132.0 (d, *J* = 22.5 Hz, 1F; *o*-Ar), −134.0 (d, *J* = 24.2 Hz, 1F; *o*-Ar), −135.2 (m, 1F; *o*-Ar), −135.6 (d, *J* = 25.9 Hz, 1F; *o*-Ar), −136.0 (m, 1F; *o*-Ar), −136.3 (m, 1F; *o*-Ar), −136.9 (m, 1F; *o*-Ar), −137.1 (m, 3F; *o*-Ar), −137.7 (d, *J* = 20.7 Hz, 1F; *o*-Ar), −138.1 (d, *J* = 24.2 Hz, 1F; *o*-Ar), −138.4 (d, *J* = 19.0 Hz, 1F; *o*-Ar), −139.2 (dd, *J* = 28.5 Hz, *J* = 18.9 Hz, 1F; *o*-Ar), −143.3 (d, *J* = 24.2 Hz, 1F; *o*-Ar), −143.6 (d, *J* = 27.6 Hz, 1F; *o*-Ar), −149.6 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −150.0 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −150.6 (t, *J* = 21.6 Hz, 1F; *p*-Ar), −151.5 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −152.8 (t, *J* = 21.6 Hz, 1F; *p*-Ar), −153.0 (t, *J* = 21.6 Hz, 2F; *p*-Ar), −153.2 (t, *J* = 20.7 Hz, 1F; *p*-Ar), −154.1 (q, *J* = 20.7 Hz, 1F; *p*-Ar), −158.5 (m, 3F; *m*-Ar), −159.9 (m, 1F; *m*-Ar), −160.0 (t, *J* = 20.8 Hz, 1F; *m*-Ar), −160.3 (t, *J* = 20.7 Hz, 1F; *m*-Ar), −160.4 (t, *J* = 20.7 Hz, 1F; *m*-Ar), −160.5 (t, *J* = 20.7 Hz, 1F; *m*-Ar), −160.7 (t, *J* = 20.7 Hz, 1F; *m*-Ar), −161.1 (t, *J* = 22.5 Hz, 1F; *m*-Ar), −161.2 (t, *J* = 21.6 Hz, 1F; *m*-Ar), −161.3 (t, *J* = 22.4 Hz, 1F; *m*-Ar), −161.6 (t, *J* = 20.7 Hz, 2F; *m*-Ar), −161.7 (t, *J* = 22.5 Hz, 1F; *m*-Ar), −161.8 (m, 1F; *m*-Ar), −163.1 (m, 1F; *m*-Ar), −164.8 ppm (t, *J* = 24.2 Hz, 1F; *m*-Ar); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 339 (41000), 466 (90000), 819 nm (93000); FAB-MS: *m*/*z*: calcd for C$_{99}$H$_{22}$F$_{45}$N$_9$Zn: 2255.06; found: 2254.94 [*M*]$^+$.

Cu^{II} complex of [42]nonaphyrin (10): NaBH$_4$ (3.8 mg, 0.1 mmol, 10 equiv) was carefully added in small portions to a stirred solution of **7** (22.5 mg, 10 μmol) in a 1:1 mixture of CH$_2$Cl$_2$ and methanol and stirring was continued for a further 30 min. The reaction was then quenched with water and the mixture was washed with brine and dried over Na$_2$SO$_4$. Removal of the solvent left a quantitative yield of the mono-Cu complex of [42]nonaphyrin **10**. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 332 (41000), 467 (84000), 818 nm (85000); FAB-MS: *m*/*z*: calcd for C$_{99}$H$_{22}$F$_{45}$N$_9$Cu: 2254.06; found: 2253.94 [*M*]$^+$.

Zn^{II}–Pd^{II} complex and Zn^{II}–Pd^{II}–Pd^{II} complex (11) of [40]nonaphyrin: Pd(OAc)$_2$ (22.4 mg, 0.1 mmol, 10 equiv) was added to a stirred solution of **6** (22.6 mg, 0.01 mmol) in a 1:10 mixture of CH$_2$Cl$_2$ and methanol at room temperature. After 2 h, the reaction mixture was washed with brine and dried over Na$_2$SO$_4$, and the solvent was removed. The residual mixture was separated by using column chromatography on silica gel (Wako gel C-400) to give the ZnPd complex (3.6 mg, 1.5 μmol, 15%) and the ZnPd$_2$ complex **11** (5.2 mg, 2.1 μmol, 21%). When the metalation was performed in the presence of sodium acetate, complex **11** was formed almost quantitatively.

Zn^{II}–Pd^{II}–Pd^{II} complex of [40]nonaphyrin (11): ^{1}H NMR (600 MHz, CDCl$_3$, 298 K): δ = 10.60 (d, *J* = 4.1 Hz, 1H; β-H), 8.53 (d, *J* = 4.1 Hz, 1H; β-H), 7.95 (t, *J* = 4.6 Hz, 1H; β-H), 7.29 (d, *J* = 4.6 Hz, 1H; β-H), 6.70 (d, *J* = 4.6 Hz, 1H; β-H), 6.21 (d, *J* = 4.6 Hz, 1H; β-H), 6.17 (d, *J* = 5.0 Hz, 1H; β-H), 5.89 (s, 1H; NH), 5.78 (d, *J* = 4.6 Hz, 1H; β-H), 5.67 (d, *J* = 5.0 Hz, 1H; β-H), 5.05 (d, *J* = 5.0 Hz, 1H; β-H), 4.85 (d, *J* = 4.6 Hz, 1H; β-H), 4.63 (s, 1H; β-H (H1 in Figure 5)), 4.40 (brs, 1H; β-H), 4.39 (t, *J* = 4.1 Hz, 1H; β-H), 3.46 ppm (brs, 1H; β-H); ^{19}F NMR (565 MHz, CDCl$_3$, 298 K): δ = −121.4 (d, *J* = 23.3 Hz, 1F; *o*-F), −123.7 (d, *J* = 21.5 Hz, 1F; *o*-F), −125.5 (m, 1F; *o*-F), −129.6 (d, *J* = 20.7 Hz, 1F; *o*-F), −129.7 (s, 1F; *o*-F), −133.2 (m, 1F; *o*-F), −133.6 (m, 1F; *o*-F), −136.9 (d, *J* = 20.7 Hz, 1F; *o*-F), −136.2 (d, *J* = 23.3 Hz, 1F; *o*-F), −136.6 (m, 1F; *o*-F), −136.7 (m, 1F; *o*-F), −136.8 (m, 2F; *o*-F), −137.0 (d, *J* = 23.3 Hz, 1F; *o*-F), −137.1 (d, *J* = 21.5 Hz, 1F; *o*-F), −138.2 (d, *J* = 22.4 Hz, 1F; *o*-F), −138.9 (d, *J* = 18.1 Hz, 1F; *o*-F), −140.0 (dd, *J* = 53.4 Hz, *J* = 26.7 Hz, 1F; *o*-F), −147.2 (s, 1F; *p*-F), −150.0 (m, 2F; *p*-F), −150.6 (m, 1F; *p*-F), −150.9 (t, *J* = 21.4 Hz, 1F; *p*-F), −151.4 (t, *J* = 20.7 Hz, 1F; *p*-F), −151.9 (t, *J* = 21.5 Hz, 1F; *p*-F), −152.1 (t, *J* = 20.7 Hz, 1F; *p*-F), −152.4 (t, *J* = 20.7 Hz, 1F; *p*-F), −153.5 (m, 1F; *m*-F), −153.4 (m, 1F; *m*-F), −158.8 (m, *J* = 23.3 Hz, 1F; *p*-F), −158.9 (t, *J* = 21.5 Hz, 1F; *p*-F), −159.3 (t, *J* = 21.5 Hz, 1F; *p*-F), −159.4 (m, 3F; *p*-F), −159.6 (m, 3F; *p*-F), −160.0 (m, 2F; *p*-F), −160.1 (m, 2F; *p*-F), −160.7 (t, *J* = 20.7 Hz, 1F; *p*-F), −160.9 (t, *J* = 20.7 Hz, 1F; *p*-F), −161.1 ppm (t, *J* = 19.8 Hz, 1F; *p*-F); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 377 (44000), 466 (66000), 649 (18000), 827 nm (63000); HR-ESI-TOF-MS: *m*/*z*: calcd for C$_{99}$H$_{15}$F$_{45}$N$_9$ZnPd$_2$: 2459.8129; found: 2459.8140 [*M*−H]$^-$.

Cu^{II}–Pd^{II} complex (12) and Cu^{II}–Pd^{II}–Pd^{II} complex (13) of [40]nonaphyrin: Pd(OAc)$_2$ (22.4 mg, 0.1 mmol, 10 equiv) was added to a stirred solution of the mono-Cu^{II} complex **7** (22.5 mg, 0.01 mmol) in a 1:10 mixture of CH$_2$Cl$_2$ and methanol under N$_2$ at room temperature. After 2 h, the reaction mixture was washed with brine and dried over Na$_2$SO$_4$, and the solvent was removed. The residual mixture was separated by using column chromatography on silica gel (Wako gel C-400) to give the CuPd$_1$ complex **12** (3.8 mg, 1.6 μmol, 16%) and the CuPd$_2$ complex **13** (11.3 mg, 4.6 μmol, 46%). When the metalation was performed in the presence of sodium acetate, complex **13** was formed almost quantitatively. Crystals of **13** suitable for X-ray crystallographic analysis were grown by means of vapor diffusion of hexane into a solution of the compound in CHCl$_3$.

$\mathrm{Cu^{II}}$–$\mathrm{Pd^{II}}$ complex of [40]nonaphyrin (12): HR-ESI-TOF-MS: m/z: calcd for $C_{99}H_{17}F_{45}N_9CuPd$: 2354.9253; found: 2354.9250 $[M-H]^-$.

$\mathrm{Cu^{II}}$–$\mathrm{Pd^{II}}$–$\mathrm{Pd^{II}}$ complex of [40]nonaphyrin (13): UV/Vis (CH_2Cl_2): λ_{max} (ε)=324 (40000), 379 (47000), 466 (55000), 630 (20000), and 838 nm (47000); HR-ESI-TOF-MS: m/z: calcd for $C_{99}H_{15}F_{45}N_9CuPd_2$: 2458.8138; found: 2458.8181 $[M-H]^-$.

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