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Porphyrinoids

Palladium(II)-Triggered Rearrangement of Heptaphyrins to N-Confused Porphyrins[**]

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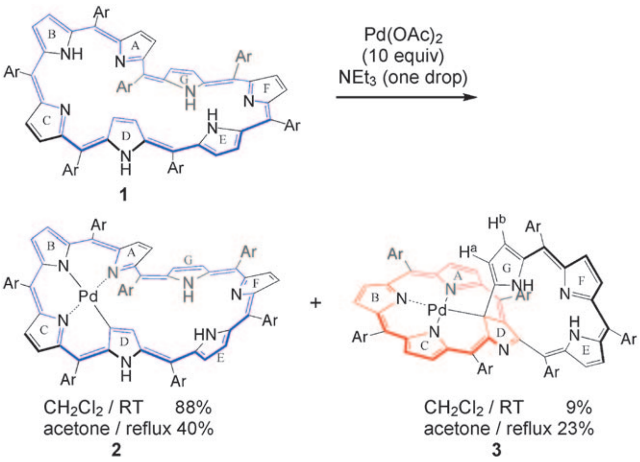
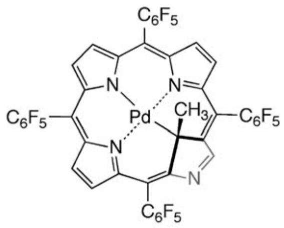
A recent surge in the chemistry of expanded porphyrins is largely due to their attractive optical, electrochemical, and coordination properties, which arise from their large π-conjugated frameworks.[1] The unique chemical reactivity of expanded porphyrins means that they often undergo metalation-induced skeletal rearrangements, as metalation reactions require specific coordination structures and expanded porphyrins have flexible electronic systems that are reactive toward such structural distortions.[2,3] The first examples of expanded porphyrins were the octaphyrins(1.1.1.0.1.1.1.0) reported by Vogel et al.,[2] which were followed by our reports on 1) the splitting reaction of a bis(Cu^{II} octaphyrin) into two Cu^{II} porphyrins,[3a,b] 2) the boron(III)-triggered splitting reaction of Cu^{II} heptaphyrins to Cu^{II} porphyrins and B^{III} subporphyrins,[3c,d] and 3) the boron(III)-induced rearrangement of a hexaphyrin(1.1.1.1.1.1) to form a hexaphyrin(2.1.1.0.1.1).[3e] These skeletal rearrangements are intriguing in making "chemical connections" between important porphyrinoids such as octaphyrins, heptaphyrins, hexaphyrins, porphyrins, and subporphyrins. Despite these results, N-confused porphyrins (NCPs), which have a key position in porphyrin chemistry,[1d,4,5] have not been included in this approach to date. Herein, we report that an NCP-type conjugated system is formed from [32]heptaphyrin(1.1.1.1.1.1.1) upon rearrangement triggered by metalation with Pd^{II} ions.

meso-Aryl-substituted [32]heptaphyrins(1.1.1.1.1.1.1) are interesting macrocycles[6] in terms of their flexible conformations,[7a] multiple N-fusion reactions,[7b] facile formation of twisted Möbius aromatic species upon protonation,[7c] formation of three-coordinated Cu^{II} complexes,[7d] and oxidative ring opening to form conjugated helical molecules.[7e] We have previously reported that a Möbius aromatic complex, **2**, was formed in 88 % yield from meso-heptakis(2,6-dichlorophenyl)-substituted [32]heptaphyrin **1** upon treatment with $Pd(OAc)_2$ in CH_2Cl_2.[7c] Careful examination of this reaction led to an isolation of brown complex **3** as a side-product in 9 % yield. When the metalation reaction was carried out in acetone, the yield of **3** was improved to 22 % at the expense of the yield of **2** (Scheme 1). High-resolution electrospray ionization time-of-flight mass spectroscopy (HR-ESI-TOF MS) indicated the parent ion peak of **3** at m/z 1659.7423 (calcd for $C_{77}H_{34}N_7Cl_{14}Pd$ $[M-H]^-$: 1659.7485). The structure of **3** was unambiguously determined by single-crystal X-ray diffraction analysis.[8] To our surprise, complex **3** contains a Pd^{II} NCP-type framework, across which a tripyrromethene unit is attached at the α- and γ-positions, C(19) and C(17), of the N-confused pyrrole (pyrrole D in Figure 1). The Pd···N(1), Pd···N(2), Pd···N(3), and Pd···C(17) distances are 2.01, 2.08, 1.99, and 2.07 Å, respectively. As seen in other NCPs, the three pyrrole units are almost planar with the mean-plane deviation of 0.07 Å, to which the inverted pyrrole D is tilted with a dihedral angle of 38.90°. The carbon atom C(17), which is bound to the Pd^{II} ion, is sp^3-hybridized.[9] The existence of aromatic NCP network is also indicated by the chemical shifts of H^a ($\delta = 1.99$ ppm) and H^b ($\delta = 4.84$ ppm) protons, which are located above the NCP ring and thus are considerably upfield-shifted because of the 18π diatropic ring current. The UV/Vis absorption spectrum of **3**



Scheme 1. Metalation of **1** with Pd^{II} ions. Ar = 2,6-dichlorophenyl.



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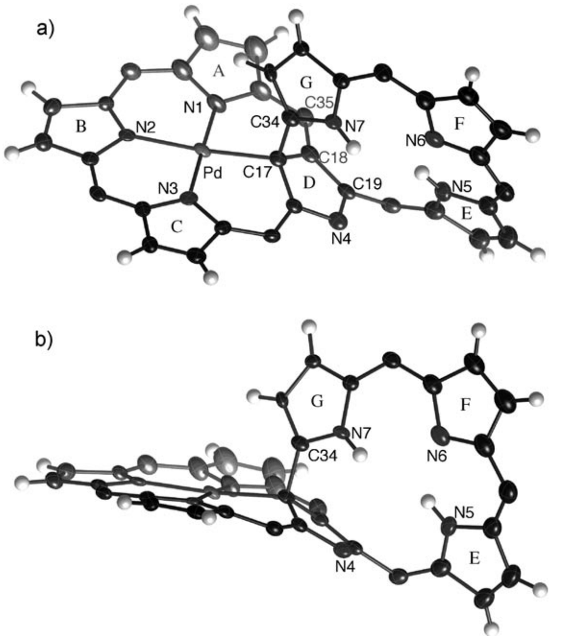


Figure 1. X-ray crystal structure of **3**: a) top view and b) side view. meso-2,6-Dichlorophenyl substituents and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

shows Soret-like bands at 419 and 449 nm, which are considerably attenuated and blue-shifted from that of heptaphyrin **1**, but are rather similar to that of the reference compound Pd^{II} NCP **4** (Figure 2).[10]

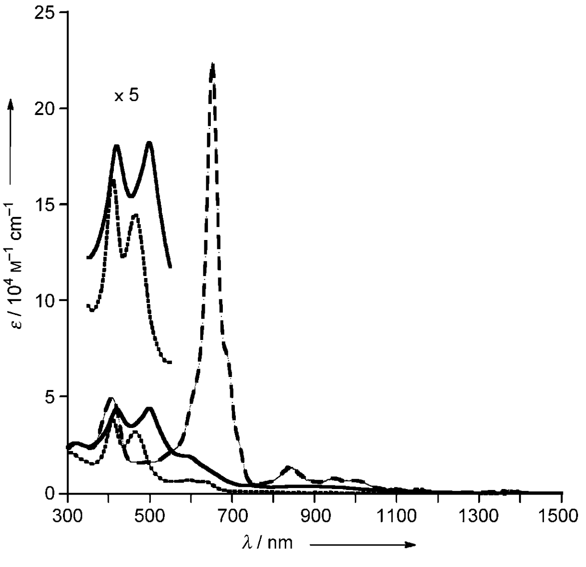
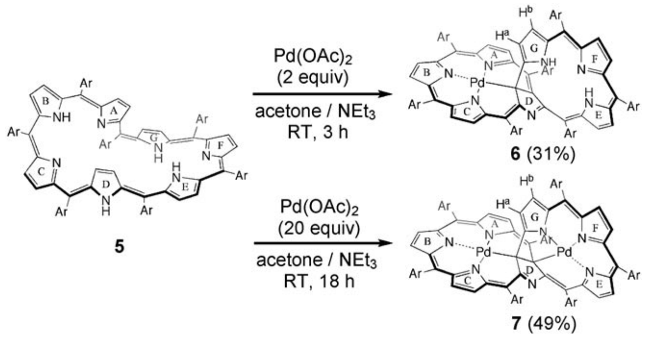


Figure 2. UV/Vis absorption spectra of **1** (–––), **3** (——), and **4** (-----) in CH_2Cl_2.



Scheme 2. Metalation of **5** with Pd^{II} ions. Ar = pentafluorophenyl.

The same rearrangement reaction proceeded for meso-heptakis(pentafluorophenyl)-substituted [32]heptaphyrin **5**, to provide either monopalladium(II) complex **6** or bispalladium(II) complex **7**, depending upon the amount of Pd^{II} salt present (Scheme 2). According to spectroscopic data, including ^{1}H NMR and UV/Vis absorption spectra, the characteristic properties of the complex **6** are analogous to those of **3**, thus suggesting an NCP-embedded framework for **6** that is practically the same as that of **3**. The structure of the complex **7** has been shown by single-crystal X-ray diffraction analysis to contain two Pd^{II} ions at the NCP-type site and the tripyrromethene site. The coordination geometry of the NCP moiety is analogous to that of **3**, in which the Pd(1)···N(1), Pd(1)···N(2), Pd(1)···N(3), and Pd(1)···C(17) distances are 1.98, 2.00, 2.00, and 2.05 Å, respectively, and the inverted pyrrole is tilted from the rest of the planar tripyrromethene part with an angle of 36.69°. The other Pd^{II} ion is bound with NNNC in a square-planar manner with Pd(2)···N(4), Pd(2)···N(5), Pd(2)···N(6), and Pd(2)···C(18) distances of 1.93, 1.93, 1.92, and 2.10 Å, respectively (Figure 3). The latter coordination causes the disruption of NCP conjugated network. Consistent with this structure, the ^{13}C NMR spectrum of **7** shows signals at $\delta = 76.09$ and 81.16 ppm that arise from the sp^3-hybridized carbon atoms C(17) and C(18), and the ^{1}H NMR spectrum indicates only marginal high-field shifts for H^a ($\delta = 4.01$ ppm) and H^b ($\delta = 6.11$ ppm) protons. The absorption spectrum of **7** is clearly different from those of **3** and **6** (see the Supporting Information).[11]

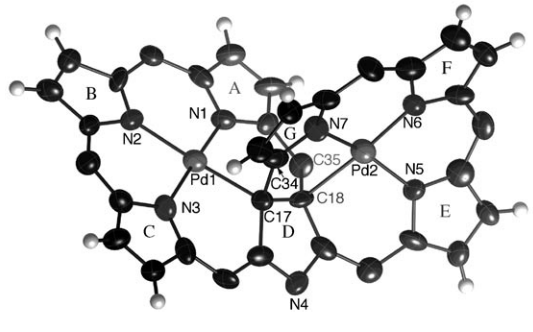
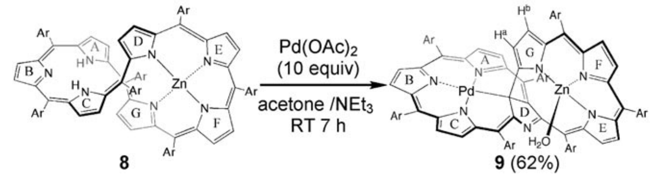


Figure 3. X-ray crystal structure of **7**. meso-Pentafluorophenyl substituents and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level.

Interestingly, a similar transformation from heptaphyrin to NCP also occurred for monozinc(II) complex **8** that has an enforced figure-eight conformation. Upon treatment with Pd(OAc)$_2$ in the presence of triethylamine in acetone, **8** underwent a rearrangement to afford the Pd^{II}–Zn^{II} hybrid complex **9** in 62% yield (Scheme 3). The structure of **9** has been also shown by X-ray diffraction analysis to have the



Scheme 3. Metalation of **8** with Pd^{II} ions. Ar = pentafluorophenyl.

same rearranged skeleton (Figure 4). The Pd^{II} NCP moiety is similar to those of the complexes **6** and **7**, in which the Pd···N(1), Pd···N(2), Pd···N(3), and Pd···C(17) distances are 2.02, 2.05, 2.03, and 2.07 Å, respectively. The distorted square-planar N, N, N, N coordination of the Zn^{II} ion in **8** was changed to a distorted tetrahedral coordination with the tripyrromethene unit and a water molecule with distances of 1.96, 1.94, 1.97, and 2.06 Å for Zn···N(5), Zn···N(6), Zn···N(7), and Zn···O, respectively. The distances between the Zn^{II} ion and C(18) and C(19) are 2.940 and 2.916 Å, which are too long for a bonding interaction. The relatively high-yielding conversion of **8** to **9** is important, as it shows the generality of the process and the possible involvement of only two pyrrole units in the rearrangement. The mechanism of this rearrangement, which apparently consists of several steps, is unclear at present. However, it is likely that coordination of Pd^{II} ions triggers the rearrangement, in which the transannular interactions and energetic stabilization associated with creation of an aromatic NCP network play important roles (see the Supporting Information for a possible mechanism).

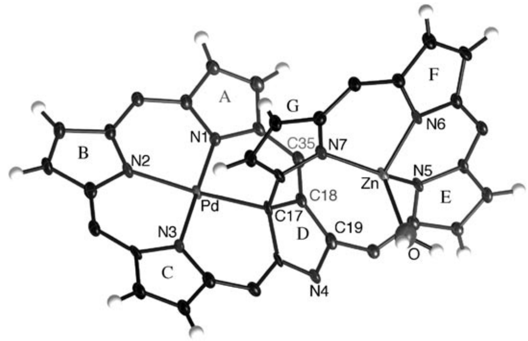


Figure 4. X-ray crystal structure of **9**. meso-Pentafluorophenyl substituents and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

In summary, we have reported the rearrangement of free-base [32]heptaphyrins(1.1.1.1.1.1.1) to Pd^{II} NCP complexes bridged by a tripyrromethene unit. This rearrangement has been demonstrated even for a monozinc(II) heptaphyrin complex with a figure-eight conformation. The occurrence of these transformations has shown that NCPs can now be considered as a member of the expanded porphyrin family.

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Keywords: heptaphyrins · metalation · palladium · porphyrinoids · rearrangement

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[8] Crystal data for **3**: $C_{82.13}H_{41.63}Cl_{17.38}N_7O_{2.38}Pd_1$ ($M_r = 1886.69$), monoclinic, space group $C2/c$ (no. 15), $a = 23.965(7)$, $b = 28.506(10)$, $c = 24.994(8)$ Å, $\beta = 107.418(6)$, $V = 16291(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.538$ g cm^{-3}, $T = 90(2)$ K, $R_1 = 0.1117$ ($I > 2\sigma(I)$), $R_W = 0.3230$ (all data), GOF = 0.988. Crystal data for **7**: $C_{81.5}H_{22}F_{35}N_7Pd_2$ ($M_r = 1977$), triclinic, space group $P\bar{1}$ (no. 2), $a = 15.0620(6)$, $b = 15.7271(5)$, $c = 17.6854(6)$ Å, $\alpha = 111.681(2)$, $\beta = 94.995(3)$, $\gamma = 111.708(3)$, $V = 3493.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.879$ g cm^{-3}, $T = 93(2)$ K, $R_1 = 0.1113$ ($I > 2\sigma(I)$), $R_W = 0.3630$ (all data), GOF = 0.920. Crystal data for **9**: $C_{85}H_{32}F_{35}N_7Pd_1Zn_1$ ($M_r = 2004$), triclinic, space group $P\bar{1}$ (no. 2), $a = 14.4760(5)$, $b = 15.0800(5)$, $c = 20.3770(8)$ Å, $\alpha = 100.1770(10)$, $\beta = 100.1180(10)$, $\gamma = 115.1180(10)$ $V = 3804.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.749$ g cm^{-3}, $T = 90(2)$ K, $R_1 = 0.0566$ ($I > 2\sigma(I)$), $R_W = 0.1387$ (all data), GOF = 0.939. CCDC 807128 (**3**), CCDC 807129 (**7**), and CCDC 807130 (**9**) 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.

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[11] Concerning the structure of **7**, one of the reviewers commented that the chemical shifts of H^a and H^b as well as C(17) and C(18) cannot be explained by solely considering the structure that contains two sp^3-hybridized carbon atoms. We suggest some contribution of the structure shown below, in which the second Pd^{II} ion is coordinated to the double bond of NCP macrocycle in a η^2 fashion.