Porphyrinoids

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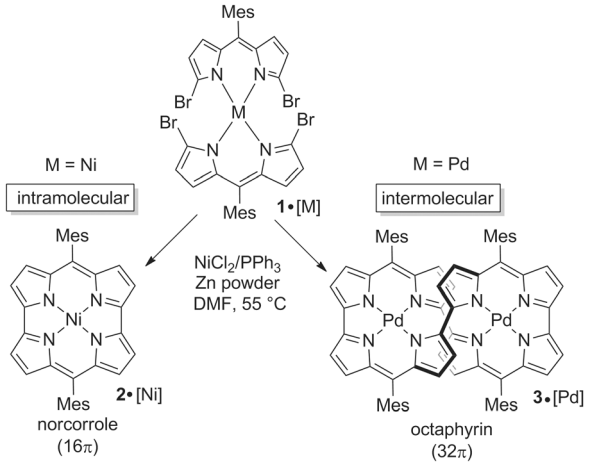
Selective Synthesis of a [32]Octaphyrin(1.0.1.0.1.0.1.0) Bis(palladium) Complex by a Metal-Templated Strategy**

*Hiromitsu Kido, Ji-Young Shin, and Hiroshi Shinokubo**

The reactivity of a substrate ligated to a metal center is often different from that of a nonligated one. In a metal complex, the metal center constrains the reaction between the ligands because of its coordination geometry and bond lengths. Such regulation by the metal center is the origin of the so-called metal-template effect, which allows selective formation of specific products. Metal-templated synthesis is a powerful tool, particularly for size-selective preparation of cyclic polyethers.[1] Unfortunately, however, a similar strategy is often not effective for polypyrrole macrocycles, namely expanded porphyrins, because of the instability of metal complexes under the acidic and oxidative reaction conditions of porphyrin synthesis.[2]

Expanded porphyrins exhibit intriguing optical and electrochemical properties as well as unique metal coordination behavior.[3] Preparation of expanded porphyrins have been achieved by several synthetic routes: 1) Direct acid-catalyzed condensation and subsequent oxidation of pyrrole and aryl aldehydes under modified Rothemund–Lindsey conditions,[4] 2) MacDonald-type coupling of oligopyrrole precursors,[5] and 3) oxidative coupling of oligopyrrole precursors such as dipyrromethanes and tripyrranes.[6] Unfortunately, however, these procedures often provide a mixture of several porphyrinic products, thus resulting in tedious chromatographic purification and low yields of the desired expanded porphyrins.

We have recently reported that nickel(0)-mediated intramolecular homocoupling of the α,α′-dibromodipyrrin nickel(II) complex **1**·[Ni] successfully provided an antiaromatic prophyrinoid nickel(II) norcorrole (**2**·[Ni]) in over 90% yield through a metal-templated strategy (Scheme 1, M = Ni).[7,8] We then investigated the effect of the metal center on the reactivity of the dipyrrin complexes and found that the α,α′-dibromodipyrrin palladium(II) complex **1**·[Pd] exclusively afforded a [32]octaphyrin(1.0.1.0.1.0.1.0) palladium(II) complex without formation of the corresponding norcorrole (Scheme 1, M = Pd). Importantly, the metal-templated strategy is not only effective for intramolecular norcorrole formation but also for intermolecular dimerization toward octaphyrin by an appropriate choice of the central metal.



Scheme 1. Metal-templated intramolecular or intermolecular homocoupling of α,α′-dibromodipyrrin complexes to norcorrole or octaphyrin.

With a the hope of obtaining the palladium(II) norcorrole complex **2**·[Pd], we attempted nickel(0)-mediated coupling of **1**·[Pd], the structure of which was solved by X-ray crystallographic analysis (Figure 1 a,b).[9] In contrast to **1**·[Ni], in which the nickel(II) center adopts a tetrahedral coordination, the two dipyrrin ligands in **1**·[Pd] are parallel to each other and the palladium center takes on a square-planar geometry.[10] This spatial arrangement of two dipyrrin units in **1**·[Pd] seemed to be ideal for the formation of a planar norcorrole complex because conversion of the geometry of the metal center is not required. Contrary to our expectation, however, none of the palladium(II) norcorrole complex **2**·[Pd] was formed and the octaphyrin(1.0.1.0.1.0.1.0) bis[palladium(II)] complex **3**·[Pd] was obtained in 35% as a single porphyrinic product upon isolation.[11] The parent mass ion peak at *m/z* 1249.3131 (calcd for $(C_{72}H_{61}N_8Pd_2)^+ = 1249.3116$ [$(M+H)^+$]) and its isotope distribution pattern of **3**·[Pd] clearly suggested formation of a bis[palladium(II)] complex from **1**·[Pd]. Other expanded porphyrins such as dodecaphyrin(1.0.1.0.1.0.1.0.1.0) were not detected in the reaction mixture. The structure of **3**·[Pd] was unambiguously elucidated by X-ray diffraction analysis (Figure 1 c,d).[12] Similar to β-alkyl-substituted octaphyrin(1.0.1.0.1.0.1.0)s, which were reported by Vogel and co-workers and Setsune et al.,[2b,5e,6a] the structure of **3**·[Pd] exhibited a figure-eight structure. We also found that treatment of **3**·[Pd] with *p*-tolylmagnesium bromide in toluene at 80 °C afforded the free

[*] H. Kido, Prof. Dr. J.-Y. Shin, Prof. Dr. H. Shinokubo
Department of Applied Chemistry
Graduate School of Engineering, Nagoya University
Nagoya, 464-8603 (Japan)
E-mail: hshino@apchem.nagoya-u.ac.jp

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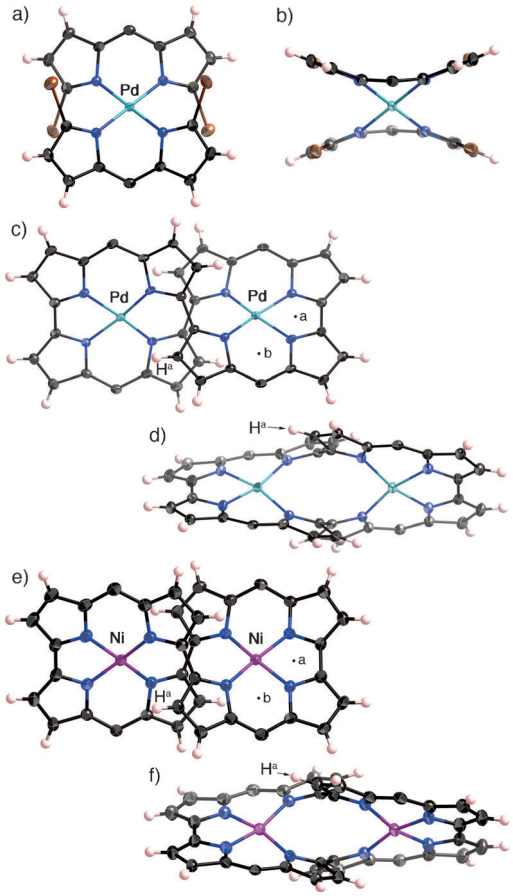
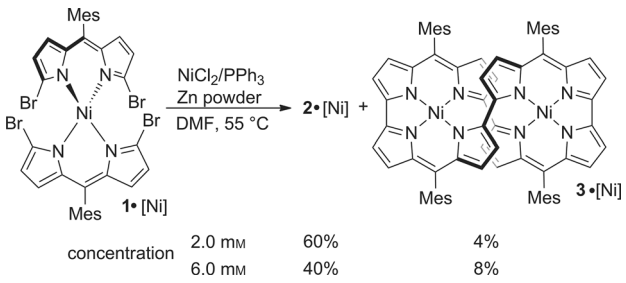


Figure 1. a) Top and b) side views of the crystal structure for **1**·[Pd]. c) Top and d) side views of **3**·[Pd]. e) Top and f) side views of **3**·[Ni]. Thermal ellipsoids are represented at 50% probability. *meso*-Mesityl groups are omitted for clarity.

base octaphyrin in 38% yield,[13] which would be a nice platform for preparation of other metal complexes.

Prompted by the finding of exclusive intermolecular homocoupling to **3**·[Pd], we reinvestigated the reaction of **1**·[Ni] and noticed the formation of a trace amount of the octaphyrin(1.0.1.0.1.0.1.0) bis[nickel(II)] complex **3**·[Ni].[14] Importantly, the yield of **3**·[Ni] was heavily dependent upon the concentration of **1**·[Ni]. At higher concentrations of **1**·[Ni] in DMF, the yields of **3**·[Ni] improved up to 8%. However, the major product was still **2**·[Ni] (Scheme 2). Unfortunately, yields of both **2**·[Ni] and **3**·[Ni] were lowered under more concentrated conditions because of the limited solubility of



Scheme 2. Concentration-dependent formation of **3**·[Ni] from **1**·[Ni].

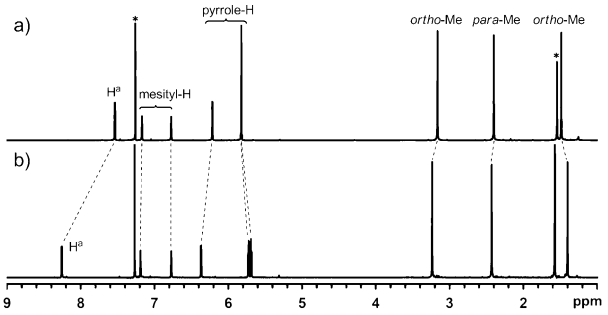


Figure 2. ^{1}H NMR spectra of a) **3**·[Pd] and b) **3**·[Ni] in $CDCl_3$.

1·[Ni] in DMF. The X-ray diffraction analysis of **3**·[Ni] revealed a figure-eight structure similar to that of **3**·[Pd] (Figure 1 e,f).[15]

Figure 2 shows the ^{1}H NMR spectra of **3**·[Pd] and **3**·[Ni] in $CDCl_3$. In both cases, four sets of doublet peaks were assigned to pyrrole protons. Interestingly, H^a (shown in Figures 1 and 2) appears in the downfield region ($\delta = 7.5$ ppm for **3**·[Pd] and $\delta = 8.3$ ppm for **3**·[Ni]). In contrast, other pyrrole β-protons are upfield shifted in comparison to those of acyclic dipyrrins, which generally resonate in the region from $\delta = 6.0$ to 7.0 ppm. Furthermore, two *ortho*-methyl groups on mesityl substituents are downfield shifted ($\delta = 3.17$ ppm for **3**·[Pd] and $\delta = 3.22$ ppm for **3**·[Ni]), while the other *ortho*-methyl protons exhibit upfield shifts ($\delta = 1.49$ ppm for **3**·[Pd] and $\delta =$ 1.38 ppm for **3**·[Ni]).[16] These changes can be explained by the paratropic ring current effect, which suggests an antiaromatic nature for these [32]octaphyrin(1.0.1.0.1.0.1.0) systems. Downfield shifted H^a and two *ortho*-methyl groups are located in the deshielded region above the π-conjugation network. The larger shift of H^a in **3**·[Ni] relative to that of **3**·[Pd] is due to the closer distance between H^a and the octaphyrin 32π-electron conjugation, thus resulting in the stronger deshielding effect upon the proton H^a. The NICS (nucleus independent chemical shift[17]) values calculated at points "a" and "b" (indicated in Figure 1) are small but all positive ($\delta = 8.2$ and 7.8 for **3**·[Pd] and $\delta = 3.9$ and 5.7 for **3**·[Ni]), thus supporting their weak antiaromatic characters (see Figure S8 in the Supporting Information).

Figure 3 shows the UV/Vis/NIR absorption spectra of **3**·[Pd] and **3**·[Ni], which have split absorption bands from $\lambda =$ 500 to 700 nm. Furthermore, weak and broad absorption bands are observed from $\lambda = 800$ to 1100 nm. These absorption features can be considered diagnostic for antiaromatic porphyrinoids, thus reflecting their small HOMO–LUMO gap and forbidden π–π transition. In line with these optical features, **3**·[Pd] and **3**·[Ni] exhibited narrow gaps between the first oxidation and reduction potentials (1.12 and 1.14 V for **3**·[Pd] and **3**·[Ni], respectively) in the electrochemical analysis by cyclic voltammetry (see Figure S7 in the Supporting Information). The electrochemical HOMO–LUMO gap is almost comparable to that of **2**·[Ni] (1.08 V). The small HOMO–LUMO gap of these octaphyrins are also supported by the DFT calculations (Figure S9 in the Supporting Information).

Selective formation of **3**·[Pd] through intermolecular coupling rather than intramolecular cyclization to norcorrole

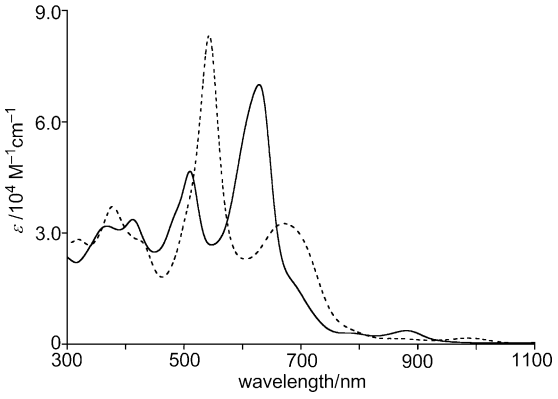


Figure 3. UV/Vis/NIR absorption spectra of **3**·[Pd] (solid line) and **3**·[Ni] (dashed line) in CH_2Cl_2.

can be accounted for by the structural difference in bis(dipyrrin) intermediates[18] resulting from the initial C–C bond formation. Figure 4 depicts the optimized structures of the plausible bis(dipyrrin) intermediates as determined by the DFT method. Because of the longer N–Pd bond (2.11 Å),

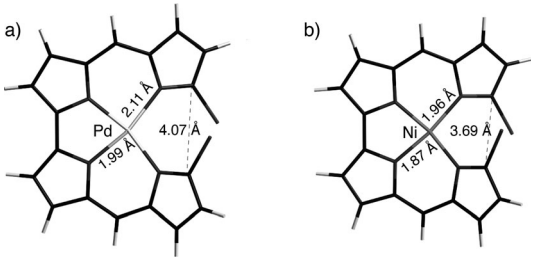


Figure 4. Calculated structures of bis(dipyrrin) intermediates at the B3LYP/631SDD level of theory.

relative to the corresponding N–Ni linkage (1.96 Å), the distance between two reacting pyrrole α-carbon atoms in the second C–C coupling is much longer in the palladium complex (4.07 versus 3.69 Å),[19] thus suggesting that the intramolecular coupling to yield the norcorrole complex is not favorable in the case of palladium(II) bis(dipyrrin) complex.

In summary, we have demonstrated that α,α′-dibromodipyrrin complexes can serve as an expeditious precursor for [32]octaphyrin(1.0.1.0.1.0.1.0) metal complexes through intermolecular homocoupling by careful choice of the central metal. These octaphyrins adopt figure-eight structures with weak antiaromatic characters, which can be confirmed by spectroscopic analyses and DFT calculations. Metal-templated synthesis of other expanded porphyrins by organometallic methods is currently under way in our group.

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[15] Crystallographic data for **3**·[Ni]: $C_{73}H_{62}Cl_2N_8Ni_2$, $M_w = 1239.63$, monoclinic, space group = $P2_1/c$ (No. 14), $a = 14.3291(7)$, $b = 23.9773(13)$, $c = 19.2668(11)$ Å, $\beta = 110.123(3)°$, $Z = 4$, $R = 0.0759$ ($I > 2.0\sigma(I)$), $R_w = 0.2192$ (all data), GOF = 1.045. CCDC 950926 (**3**·[Ni]) contains 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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