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New Synthetic Strategy for Diporphyrins: Pinacol Coupling–Rearrangement

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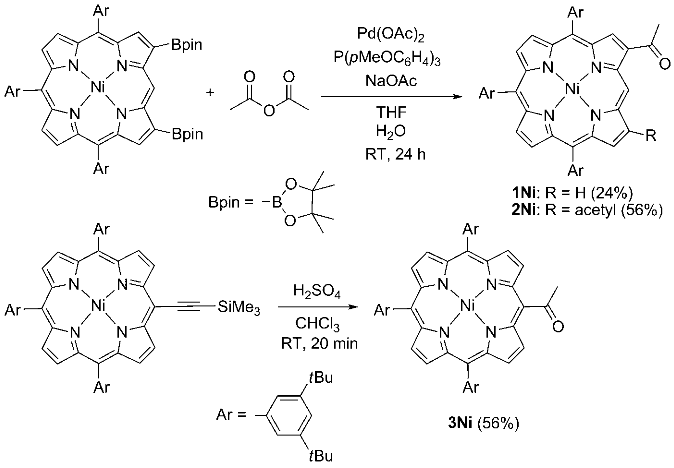
Numerous kinds of porphyrin oligomers have been synthesized and explored as biomimetic models for photosynthetic systems and oxygen reducing enzymes, photonic materials, and functional molecular devices.[1–3] In particular, porphyrin dimers linked by various spacers have been synthesized as very attractive motifs to understand the dipole and electronic exchange interactions between the adjacent porphyrin subunits or to create building blocks for larger porphyrin arrays.[1,4] Recently, we have reported the synthesis of β,β′-doubly 2,6-pyridylene-bridged Ni^{II} porphyrin belts by using the Suzuki–Miyaura coupling reaction.[4a] Their remarkably bent structures have encouraged the synthetic extension to a cyclic porphyrin nanobarrel.[4b]

In creating new porphyrin dimers of interest, it is important to develop a novel strategy for connecting two porphyrin monomer units. We envisioned that SmI$_2$-mediated pinacol coupling of acyl porphyrin would provide a reliable and unique tool.[5] This was indeed the case for a β-acetyl Ni^{II} porphyrin, which was subjected to pinacol coupling to provide a diol. The diol underwent a rearrangement under acidic conditions to yield a pinacol-type diporphyrin, which underwent further dehydrative rearrangement to provide a conformationally constrained diporphyrin, which is doubly bridged by methylene groups and represents a rare case in the literature.[6,7]

The starting acetylated porphyrins were prepared as illustrated in Scheme 1. Although a few synthetic approaches to acetyl porphyrins have already been reported,[8] we have employed different methods for the efficient synthesis of β- and *meso*-acetyl porphyrins. For the synthesis of β-acetyl porphyrins, β,β′-diboryl Ni^{II} porphyrin was treated with acetic anhydride in the presence of catalytic amounts of palladium acetate and tris(4-methoxyphenyl)phosphine in THF containing a small amount of water, which provided β-acetyl Ni^{II} porphyrins **1Ni** and **2Ni** in 24 and 56% yields, respectively (Scheme 1).[9] For a *meso*-acetyl porphyrin, a *meso*-trimethylsilylethynyl Ni^{II} porphyrin was exposed to sulfuric acid in chloroform, which resulted in the formation of **3Ni** in 56% yield (Scheme 1).



Scheme 1. Synthesis of acetyl porphyrins **1Ni**, **2Ni**, and **3Ni**.

The X-ray crystallographic analyses unambiguously elucidated the structures of **2Ni** and **3Ni** (see the Supporting Information).[10] Interestingly, the acetyl group at the *meso* position in **3Ni** is almost perpendicular (81.5°) to the porphyrin framework, whereas the acetyl groups at the β positions in **2Ni** are nearly coplanar (2.0 and 10.5°), which reflects different steric environments at the *meso*- and β positions.

Reaction of **1Ni** with SmI$_2$ in THF quantitatively provided diporphyrinated pinacol analogue **4Ni**. However, **4Ni** was unstable and gradually oxidized back into **1Ni** in the air. We therefore subjected **4Ni** immediately to pinacol rearrangement conditions without further purification, which was done through treatment of crude **4Ni** with BF$_3$·OEt$_2$ to give **5Ni** in high yield (Scheme 2). It is worth noting that the migration of a bulkier porphyrin subunit was preferred over that of methyl group and that no rearrangement proceeded in the reaction of freebase porphyrin with BF$_3$·OEt$_2$, in which the protonation of the inner nitrogen atoms would occur to prohibit the rearrangement. Curiously, no conversion was observed in the reaction of *meso*-acetyl porphyrin **3Ni** with SmI$_2$ under similar pinacol coupling conditions.

The parent mass ion peak of **5Ni** was observed at $m/z = 1952.0371$ (calcd for $C_{128}H_{148}N_8Ni_2ONa$: 1952.0375 $[M+Na]^+$) in its high-resolution electrospray-ionization time-of-flight (HR-ESI-TOF) mass spectrum, indicating the formation of a dimeric product. The ^{1}H NMR spectrum of **5Ni** showed one singlet signal derived from the *meso* proton at $\delta = 9.84$ ppm and two singlet signals from the methyl groups at $\delta = 3.28$ and 2.61 ppm. The UV/Vis absorption spectrum

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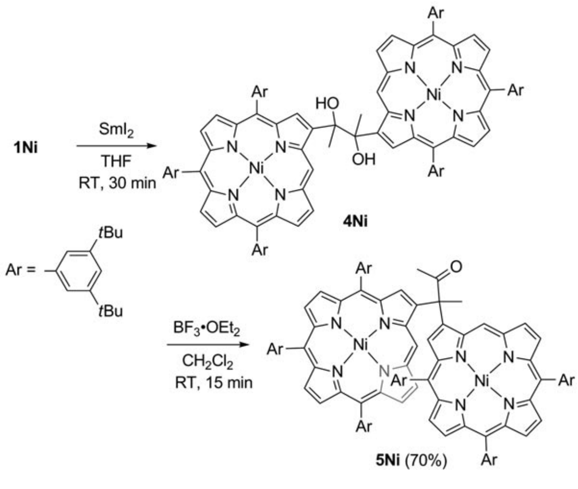
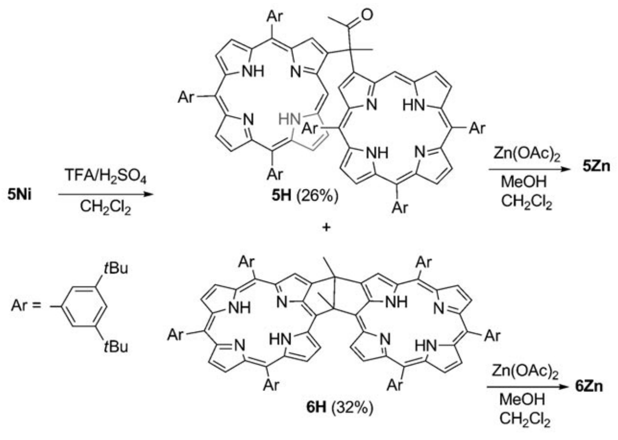


Scheme 2. Synthesis of **5Ni**.

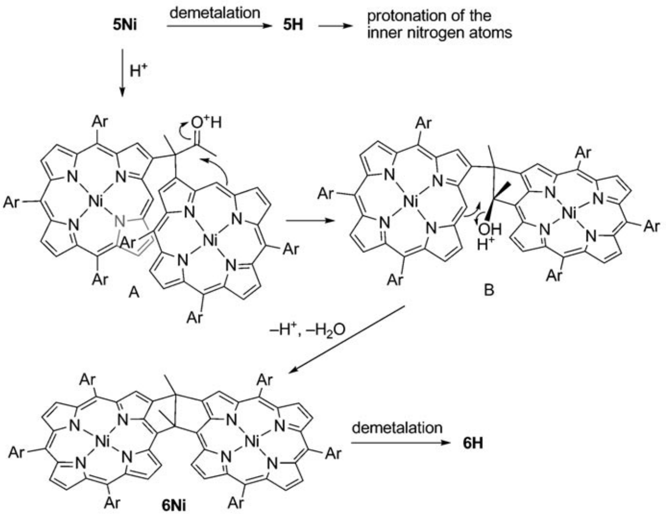
of **5Ni** displays a non-split but perturbed Soret band probably due to exciton coupling of the two porphyrins held in a skewed arrangement (see the Supporting Information).

Treatment of **5Ni** with concentrated sulfuric acid and trifluoroacetic acid for demetalation gave two compounds; one was the expected pinacolone diporphyrin, **5H**, and the other was surprisingly a tetrahydropentalene-fused diporphyrin, **6H** (Scheme 3). These two dimers were easily separated by silica gel column chromatography. The HR-ESI-TOF mass spectrum of **6H** displayed the parent ion peaks at $m/z = 1800.2116$ (calcd for $C_{128}H_{151}N_8$: 1800.2062 $[M+H]^+$), whereas that of **5H** displayed a peak at $m/z = 1818.2232$ (calcd for $C_{128}H_{153}N_8O$: 1818.2162 $[M+H]^+$). This result indicates the occurrence of dehydration reaction and demetalation in the transformation from **5Ni** to **6H**. The ^{1}H NMR spectrum of **6H** revealed a disappearance of the *meso* proton. The ^{13}C NMR spectrum displayed distinct two signals ($\delta = 82.85$ and 57.78 ppm) derived from two carbon atoms at the benzyl-like positions between the two porphyrin subunits.



Scheme 3. Synthesis of **5H**, **5Zn**, **6H**, and **6Zn**. TFA = trifluoroacetic acid. Ac = acetyl.

A plausible reaction mechanism is shown in Scheme 4. Since **5H** did not rearrange under the same acidic conditions, we thought that the intramolecular Friedel–Crafts reaction preceded the demetalation; the protonation of the carbonyl oxygen atom followed by nucleophilic attack of the Ni^{II} porphyrin subunit toward the activated acetyl group (Scheme 4, A) would form a fused cyclopentene skeleton. The subsequent nucleophilic attack along with the elimination of water (Scheme 4, B) should construct a doubly fused tetrahydropentalene structure.



Scheme 4. A plausible reaction mechanism.

Zinc metalations of **5H** and **6H** were conducted to obtain the single crystals of these dimers for X-ray analyses (Scheme 3). The X-ray crystallographic analysis of **5Zn** unambiguously elucidated its dimeric structure, which has a skewed arrangement of the two porphyrin rings (Figure 1).[11] The two planes through the four nitrogen atoms of the porphyrins form a dihedral angle of 75°. This structural feature is similar to that of the hydroxymethylene-bridged porphyrin dimer reported by Senge.[6a] As for **6Zn**, the final structural proof was obtained from its single-crystal X-ray diffraction analysis (Figure 2),[11] which revealed a tetrahydropentalene-fused gable structure with a dihedral angle of 99°.

The UV/Vis absorption spectra of **5** and **6** can be explained in terms of the excitonic coupling theory;[12,13] the changes in the absorption spectra would result from the difference of the spacial arrangement of porphyrin subunits in **5** and **6**. The Soret band of **5H** is split to a red-shifted band at 429 nm and the original band at 419 nm along with a blue-shifted shoulder around 400 nm (Figure 3). The red- and blue-shifted absorption bands of **5H** are due to J- and H-type dipole–dipole interactions, respectively. On the other hand, the UV/Vis absorption spectrum of **6H** displays a Soret band at 412 nm and a considerably broader Soret band at 436 nm, which have been assigned due to H- and J-type dipole–dipole interactions, respectively. The fluores-

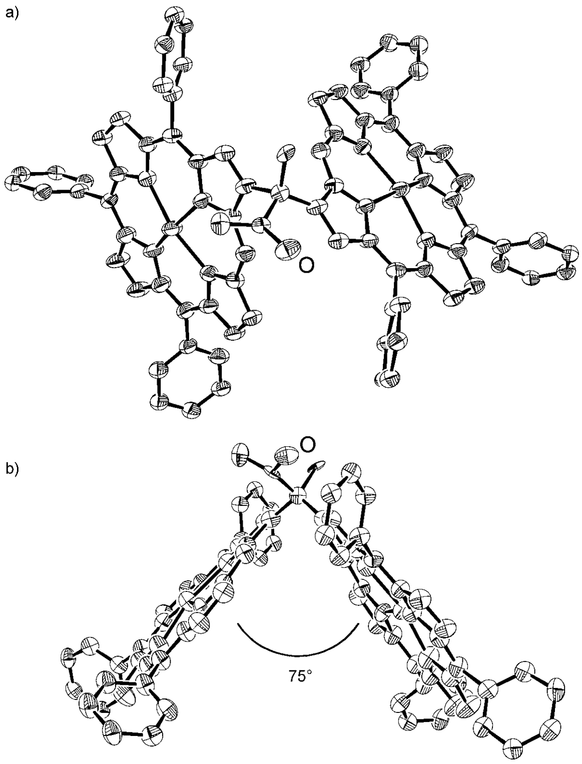


Figure 1. X-ray crystal structure of **5Zn**. a) Top and b) side view. *tert*-Butyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30 % probability level.

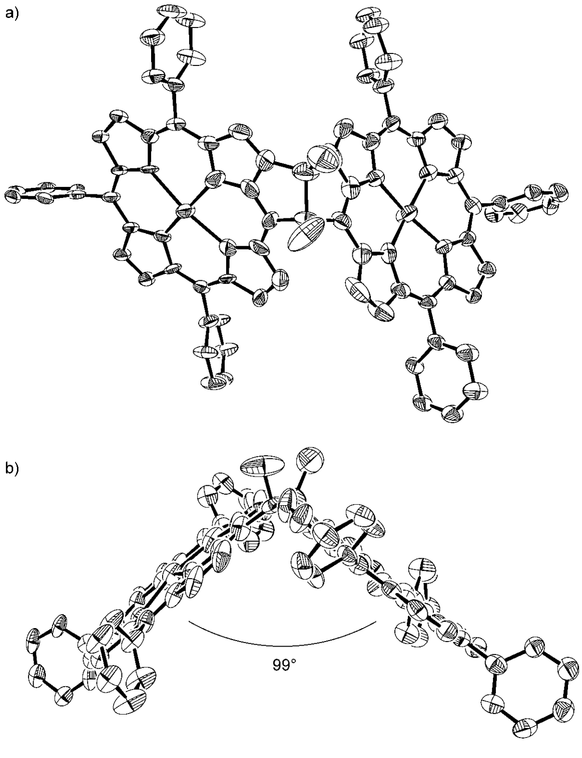


Figure 2. X-ray crystal structure of **6Zn**. a) Top and b) side view. *tert*-Butyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30 % probability level.

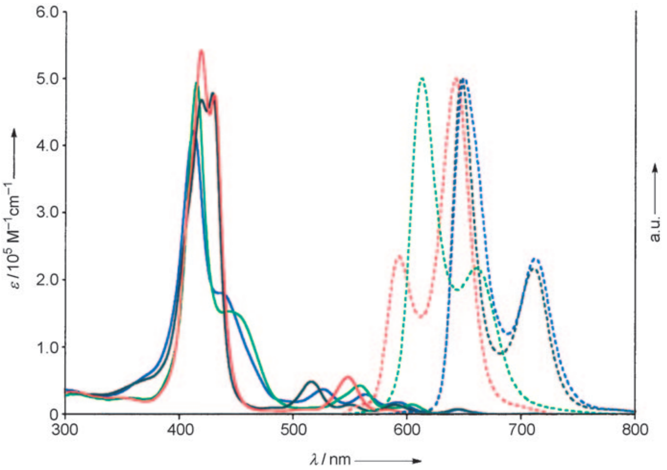


Figure 3. UV/Vis absorption (solid lines) and fluorescence (dashed lines) spectra in CH_2Cl_2 (black line = **5H**, red line = **5Zn**, blue line = **6H**, green line = **6Zn**). The excitation wavelengths are 428 (for **5H**), 419 (for **5Zn**), 412 (for **6H**), and 415 nm (for **6Zn**). The fluorescence quantum yields (Φ_F) are 6.3 (for **5H**), 2.7 (for **5Zn**), 7.7 (for **6H**), and 3.9 % (for **6Zn**).

cence spectra of **5H** and **6H** are shown in Figure 3. The fluorescence quantum yield of **6H** ($\Phi_F = 7.7\,\%$) is slightly higher than that of **5H** ($\Phi_F = 6.3\,\%$), probably because of its rigid structure. A similar tendency was observed in the spectra of **5Zn** and **6Zn**.

In summary, we have accomplished the palladium-catalyzed β-acetylation of β-boryl Ni^{II} porphyrins, the pinacol coupling of β-acetyl Ni^{II} porphyrin with SmI_2, and the acid-catalyzed pinacol–pinacolone rearrangement and further acid-catalyzed dehydrative rearrangement of a pinacolone-type diporphyrin to a tetrahydropentalene-fused diporphyrin. In the final diporphyrin system, the two porphyrins are held close in a conformationally restricted manner but electronically insulated, which will be useful for studies on intramolecular electron transfer and energy transfer reactions.

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Keywords: acetylation • nickel • pinacol coupling–rearrangement • porphyrin • samarium

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[10] Crystallographic data for **2Ni**: $C_{67.50}H_{77}Cl_{4.50}N_4NiO_2$, $M_w = 1194.57$, monoclinic, space group $C2/c$ (No. 15), $a = 34.146(6)$, $b = 12.030(3)$, $c = 31.387(5)$ Å, $\beta = 104.821(6)°$, $V = 12464(4)$ Å^3, $Z = 8$, $D_{calc} = 1.273$ g cm^{-3}, $T = 123(2)$ K, $R = 0.0494$ ($I > 2.0\sigma(I)$), $R_w = 0.1372$ (all data), GOF = 1.040 ($I > 2.0\sigma(I)$). Crystallographic data for **3Ni**: $C_{64}H_{74}N_4NiO$, $M_w = 973.98$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.132(3)$, $b = 16.073(4)$, $c = 16.124(5)$ Å, $\alpha = 65.135(9)$, $\beta = 80.400(9)$, $\gamma = 71.468(9)°$, $V = 2702.7(12)$ Å^3, $Z = 2$, $D_{calc} = 1.197$ g cm^{-3}, $T = 123(2)$ K, $R = 0.0639$ ($I > 2.0\sigma(I)$), $R_w = 0.1645$ (all data), GOF = 1.032 ($I > 2.0\sigma(I)$). CCDC-817793 (**2Ni**) and 817790 (**3Ni**) 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

[11] Crystallographic data for **5Zn**: $C_{131.24}H_{157.73}N_8O_{4.24}Zn_2$, $M_w = 2045.84$, monoclinic, space group $P2/n$ (No. 13), $a = 24.1755(9)$, $b = 9.6509(4)$, $c = 28.7211(10)$ Å, $\beta = 92.8009(17)°$, $V = 6693.1(4)$ Å^3, $Z = 2$, $D_{calc} = 1.015$ g cm^{-3}, $T = 93(2)$ K, $R = 0.1051$ ($I > 2.0\sigma(I)$), $R_w = 0.3401$ (all data), GOF = 1.027 ($I > 2.0\sigma(I)$). Some unassigned electron density due to severely disordered solvent was removed by using the utility SQUEEZE in the PLATON software package.[14] Crystallographic data for **6Zn**: $C_{137}H_{159}N_8O_{4.50}Zn_2$, $M_w = 2120.46$, triclinic, space group $P\bar{1}$ (No. 2), $a = 15.724(6)$, $b = 21.299(8)$, $c = 21.985(8)$ Å, $\alpha = 69.733(7)$, $\beta = 76.903(8)$, $\gamma = 69.360(7)°$, $V = 6418(4)$ Å^3, $Z = 2$, $D_{calc} = 1.097$ g cm^{-3}, $T = 90(2)$ K, $R = 0.1067$ ($I > 2.0\sigma(I)$), $R_w = 0.3417$ (all data), GOF = 0.881 ($I > 2.0\sigma(I)$). CCDC-817792 (**5Zn**) and 817791 (**6Zn**) 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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