meso-Diketopyripentaphyrin and Diketopyrihexaphyrin as Macrocyclic Tripyrrinone Ligands for Ni^{II} Ions.

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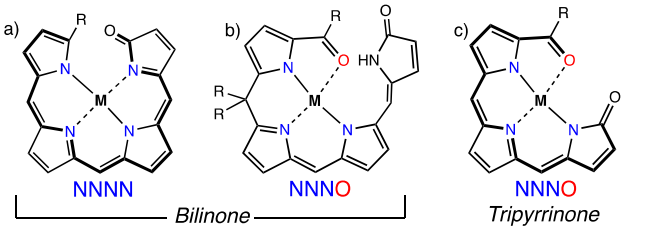
Abstract: We report novel expanded porphyrins with pyridine rings and two neighboring carbonyl groups, which allow Ni^{II} ions to coordinate to the tripyrrinone-type NNNO coordination structure with Ni-O bonds. The selectivity of tripyrrinone is superior to other pyrrolic or pyridinic cavities of expanded porphyrins. Introduction of α-carbonyl pyridine next to the tripyrrolic conjugated structure is a powerful strategy for regioselective metalation of flexible expanded porphyrinoids.

Release of metal ions by oligopyrrolic units induced by cleavage of porphyrin metal complexes is a very crucial phenomena in the degradation of heme and chlorophyll.[1] Bilinones, which are important biopigments, can be obtained by oxidative ring-opening of porphyrins. In the oxidative reaction, the porphyrins are cleaved into bilinones, a linear conjugated tetapyrrolic compound with two oxygenated terminal α-positions. However, bilinones sometimes coordinate to metal ions only in an NNNN coordination manner (Figure 1a).[2] Similar bilinones are known as the photo-oxidation products of *meso*-aryl porphyrinoids.[3] In the degradation proces, the *meso*-pyrrole C–C bond was cleaved with molecular oxygen to furnish a *meso*- and α-oxygenated linear tetrapyrrolic unit and it sometimes acts as an NNNO ligand.[3a,b] (Figure 1b)

As such an NNNO ligand, tripyrrinone consisting of a conjugated linear tripyrrolic moiety with an adjusting carbonyl group acts as a tetradentate ligand with a helix-like NNNO coordination site (Figure 1c). While similar NNNO-coordination systems are produced by oxidation of tripyrrolic ligands,[4] the copper(II) complex of the N-confused porphyrin induces oxidative cleavage to produce a fully conjugated tripyrrinone-metal complex.[5] Until today, tripyrrinone units have been synthesized by oxidation of N-confused porphyrin metal complexes (Scheme 1). The tripyrrinones are capable of coordinating to various metal ions, such as Zn^{II}, Ni^{II}, Pd^{II}, and Pt^{II} (Scheme 1).



Scheme 1. Synthesis of the tripyrrinone-metal complex and its metal conversion.

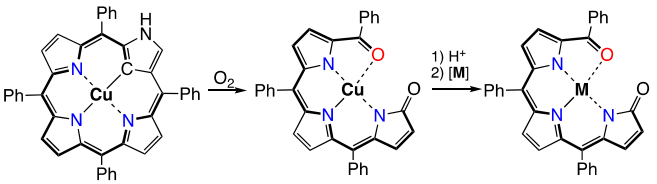


Figure 1. Linear conjugated oligopyrrolic units as metal ligands

The coordination ability of the free tripyrrinone ligand has not been extensively investigated compared with other pyrrolic ligands in macrocyclic molecules. The NNNO coordination pocket of tripyrrinone unit is attractive even in the expanded porphyrins containing many NNNN of NNNC-type coordination pockets,[6] which sometimes induces poor regioselective metalation into a specific structure.[7] In addition, oxidative nickel metalation of octaphyrin(1.1.1.1.1.1.1.1)s provided some circular tripyrrinone moieties by rearrangement, but the yield and selectivity was very poor.[7b]

In this study, we investigate *meso*-oxygenated pyriporphyrins which contain the tripyrrinone moiety in their macrocyclic structure. The α-carbonyl oligopyrrolic units behave like the tripyrrinone ligand with a macrocyclic structure and the oligopyrrolic unit is cyclized and stabilized the pyridyl group. These NNNO tripyrrinone units effectively capture nickel ions to produce tripyrrinone-nickel(II) complexes in preference to tetrapyrrolic NNNN coordination.

Pyriporphyrins, in which the pyridine moieties are installed into porphyrinoids, are homologues of porphyrin. Pyriporphyrins are known as NNNN tetradentate ligands because of their four inward-pointing nitrogen atoms.[8] In addition, in the synthetic procedure of *meso*-free pyriporphyrins, *meso*-carbon was sometimes oxygenated.[8a] In these molecules, the aromaticity of the 6π pyridine rings is often preferred to macrocyclic conjugation. Expanded pyriporphyrins, as expanded analogues of pyriporphyrins[9], have also been employed as ligands of some metal complexes.[9a,c] In the course of synthesis of *meso*-unsubstituted expanded pyriporphyrins, we obtained *meso*-oxygenated expanded pyriporphyrins (expanded diketopyriporpyhrins). Therefore, we investigated the structural characteristics of the expanded pyriporphyrin units.

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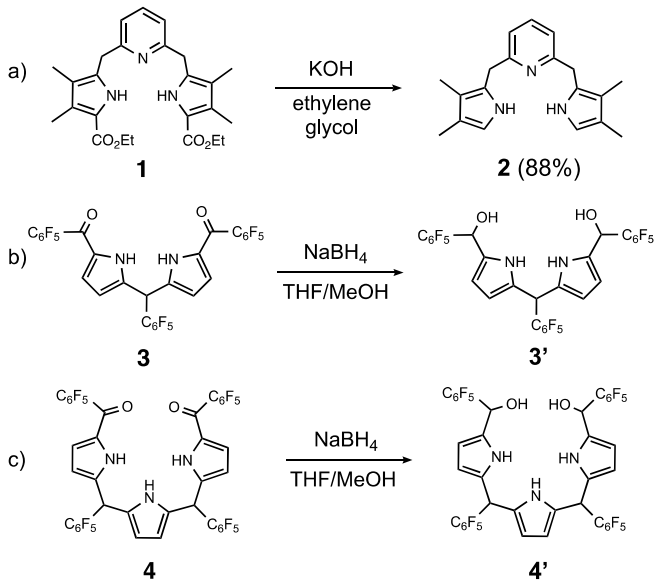
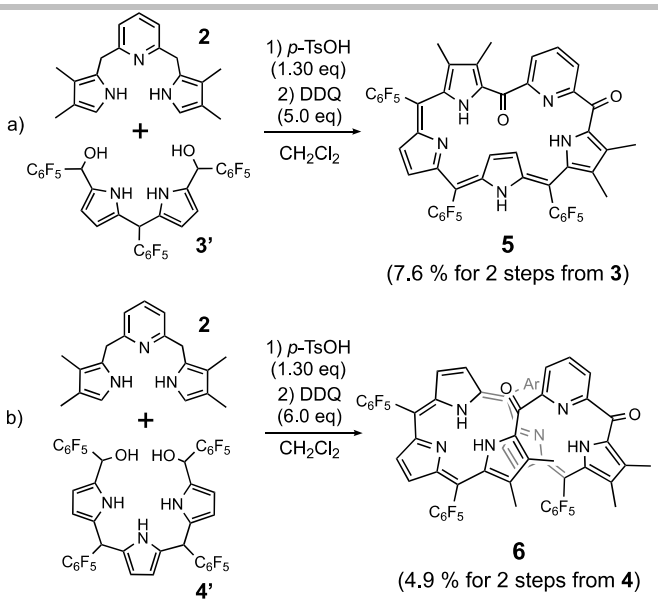
The expanded diketopyriporphyrins were prepared by acid-catalyzed condensation of 2,6-bis((pyrrol-2-yl)methyl pyridine **2** and petafluorophenyl substituted dipyrromethene dicarbinol **3'** following the previously reported method.[10] 2,6-bis((Pyrrol-2-yl)methyl pyridine unit **2** was prepared by decarboxylation of ethyl ester **1**[11] with potassium hydroxide (Scheme 2a). **2** and dipyromethane dicarbinol **3'**, which have been furnished by reduction of acyl precursor **3** with $NaBH_4$ (Scheme 2b) were condensed with 1.3 equiv of *p*-toluenesulfonic acid monohydrate as catalyst in dichloromethane in a N_2 atmosphere (Scheme 3a). In the reaction, excess *p*-toluenesulfonic acid was required for acid-catalyzed condensation overcoming the basicity of the pyridine. The reaction mixture was oxidized with excess (5.0 equiv) of DDQ to afford *meso*-oxygenated pentaphyrin **5**. The usual workup and separation by silica-gel column chromatography provided compound **5** as a green solid in 7.6% yield. High-resolution electrospray ionization time-of-flight mass spectroscopy (HR ESI-TOF-MS) gave the parent ion peak of **5** at *m/z* = 986.1612 (calcd for $C_{48}H_{22}F_{15}N_5O_2$: 986.1587). The ^{1}H NMR spectrum of **5** in $CDCl_3$ contained four doublets at δ = 8.15, 6.70, 6.63, and 6.39 ppm owing to outer pyrrole β protons, suggesting an asymmetric structure. The peaks derived from NH protons were observed at 12.50, 9.06, and 6.48 ppm, indicating the two NHs and one NH with and without hydrogen bonding, respectively. The structure of diketopyripentaphyrin **5** was finally unambiguously confirmed by X-ray crystallographic analysis of the crystals of **5** obtained by slow diffusion of heptane into its ethyl acetate solution. The X-ray crystallographic structure[12] showed a relatively planar, asymmetric trapezoid structure with two oxygenated *meso*-carbon atoms. The inward- and outward-pointing C–O bond lengths were 1.231(6) and 1.243(6) Å, respectively, strongly indicating their C=O double bond character (see supporting information).



Scheme 2. Preparations of the precursors of expanded diketopyripentaphyrin and diketopyrihexaphyrin..



Scheme 3. Synthesis of diketopyripentaphyrin **5** and diketopyrihexaphyrin **6**.

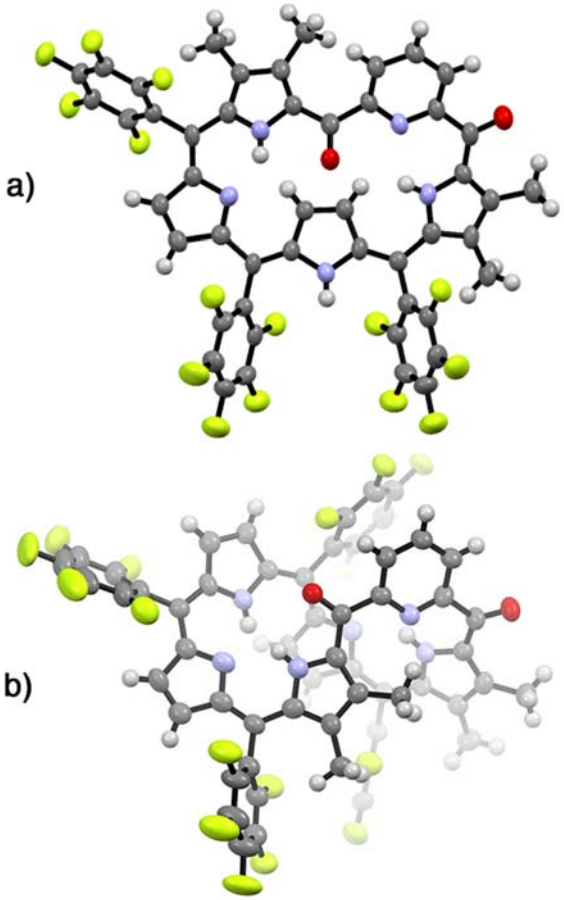
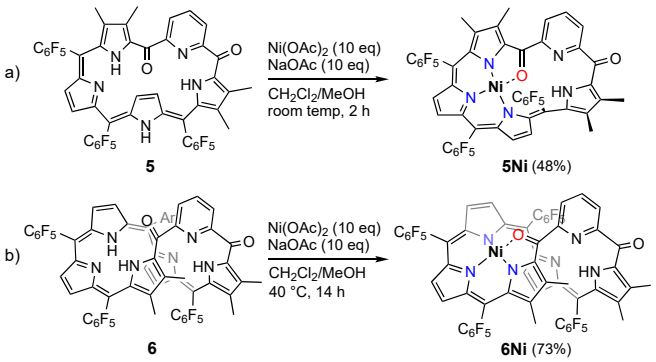


Figure 2. X-ray crystal structures of a) diketopyripentaphyrin **5** and b) diketopyrihexaphyrin **6**. For **6**, one of two slightly different independent structures in the asymmetric unit is shown. The solvent molecules are omitted in the side view. The thermal ellipsoids are shown at the 50% probability level.

Diketopyrihexaphyrin **6** was also synthesized by similar acid catalyzed condensation of **2** and tripyrrane dicarbinol **4'**. The mixture was oxidized with 6.0 equiv. of DDQ. After the usual workup and chromatographic separation followed by recrystallization, pure pyrihexaphyrin **6** was obtained as a red solid in 13% yield. The HR-ESI-TOF-MS of **6** gave *m/z* =

1229.1720 (calcd for $C_{59}H_{24}F_{20}N_6O_2$: 1229.1741). The ^{1}H NMR spectrum of **6** in $CDCl_3$ showed six doublets at δ = 6.22, 6.66, 6.73, 6.74-6.76, and 6.84 ppm owing to outer pyrrole β protons, indicating an asymmetric structure. The peaks derived from NH protons were observed at 10.92, 13.28, and 13.52 ppm, indicating that all three NH protons were hydrogen bonding. X-ray crystallographic analysis of **6**[13] showed a characteristic figure-of-eight conformation. The structure contained N-NH-N and NH-N-NH sets of hydrogen bonding. Their C=O double bond character was also confirmed by their lengths of 1.213(8)–1.238(8) Å (see supporting information).

These *meso*-oxo species were deduced to be generated by oxidation of the *meso*-position with DDQ. *meso*-Oxygenated porphyrins in general are degradated by oxidation into linear conjugated oligopyrroles with opening the cyclic structure.[2,14] However, in our system, ring-opening or decomposition seems to be suppressed by the electron-deficient pyridine unit, similar to *meso*-ketopyriporphyrins.[8a] The conjugation structure of the keto-unit is similar to the *meso*-alkylidene expanded porphyrins reported by Lee *et al*.[15] In contranst, our diketopyriporphyrins **5** and **6** have electronegative oxygen atoms that can coordinate to metal ions.



Scheme 4. Synthesis of 1) diketopyripentaphyrin **5Ni** and 2) diketopyrihexaphyrin **6Ni**.

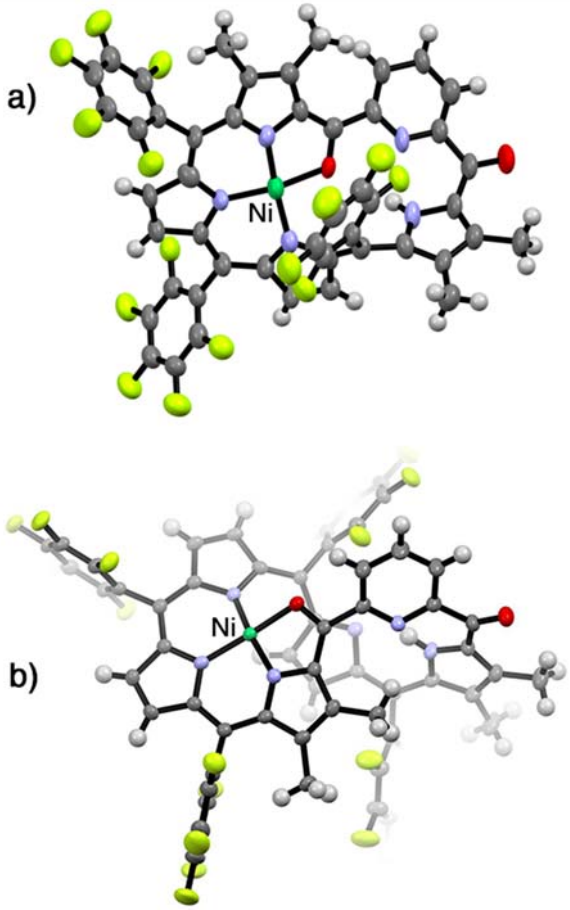


Figure 3. X-ray crystal structures of a) diketopyripentaphyrin-Ni^{II} complex **5Ni** and b) diketopyrihexaphyrin-Ni^{II} complex **6Ni**. Ones of two slightly different independent structures in the asymmetric unit are shown. The solvent molecules are omitted in the side view. The thermal ellipsoids are shown at the 50% probability level.

With the expanded porphyrins in hand, we investigated metalation of diketopyripentaphyrin **5** and diketopyrihexapyhrin **6**. When **5** or **6** was treated with 10 equiv. of nickel acetate in dichloromethane/methanol solution to give the corresponding nickel complex **5Ni**(48%) or **6Ni**(73%), respectively (Scheme 4). These reactions proceed under milder conditions (at room temperature for **5** or 40 °C for **6**) comparing with the Ni metalation of *meso*-pentafluorophenyl substituted hexaphyrin(1.1.1.1.1.1) which requires 12 h refluxing in toluene solution to produce the Ni^{II} complex with the NNNC coordination structure.[16] Therefore, the tripyrrinone unit of diketopyrihexaphyrin more easily accomodates to the Ni ion than that of simple hexaphyrins. The HR-ESI-TOF-MS spectra of **5Ni** and **6Ni** showed peaks at *m/z* = 1040.0689 (calcd for $C_{48}H_{20}F_{15}N_5O_2Ni_1$: 1040.0653) and 1285.0917 (calcd for $C_{59}H_{22}F_{20}N_6O_2Ni_1$: 1285.0928), suggesting mono-Ni(II) metalation of the free-bases. The ^{1}H NMR spectrum of **5Ni** shows signals of four ß-protons at 6.76-7.47 ppm derived from the unaffected pyrrole units. The ^{1}H NMR spectrum of **6Ni** also exhibited six signals of ß-protons at 6.10–7.28 ppm, which suggests that the ß-carbons were also intact and did not form C–Ni bonds.

X-ray crystallographic analysis supports their tripyrrinone-type NNNO-coordination structure. Single crystals of **5Ni** produced by slow diffusion of water into its acetone solution were analyzed by X-ray crystallographic analysis[17] (Figure 3a). In the X-ray crystal

structure, one pyrrole unit was inverted into inward-pointing to coordinate nickel(II) ion. The pyridine-nitrogen atom does not coordinate to the metal ion, although it is hydrogen bonded to opposite nitrogen atom. The lengths of the Ni–N bonds were in the range of 1.782(5)–1.855(5) Å, suggesting typical coordination of the nitrogen atoms to the nickel ion. The lengths of Ni-O bond lengths were 1.872(4) and 1.906(4) Å. The coordinating C–O bond lengths were 1.293(6) and 1.307(7) Å. These are slightly longer than those of the other non-coordinationg C=O double bonds (1.234(6) and 1.238(7) Å), but definitely shorter than that of typical C–O single bond (1.43 Å). For pyrihexaphyrin[18] **6Ni** (Figure 3b), the complete figure-of-eight structure was preserved through metalation. The Ni–N and Ni–O bond lengths are in the ranges of 1.799(3)–1.839(3) and 1.893(2)–1.897(2) Å, respectively. The C–O bond lengths of coordinating carbonyl groups were 1.289(4) and 1.284(4) Å, which are also slightly longer than that of double bond, suggesting the weak double bond character of the metal-coordinating keto-group.

The UV/Vis absorption spectra of **5**, **5Ni**, **6**, and **6Ni** are shown in Figure 4. The similarity of absorption spectra of **5** and **6** to those of *meso*-alkylidene expanded porpyhrins[15a] warrants the cross-conjugated conjugatin circuits of them. The absorption bands of **5Ni** and **6Ni** are red shifted compared with the free bases **5** and **6**. These bathochromic shifts agree with those of known tripyrrinone ligands, but the whole spectra are not drastically changed after metalation.

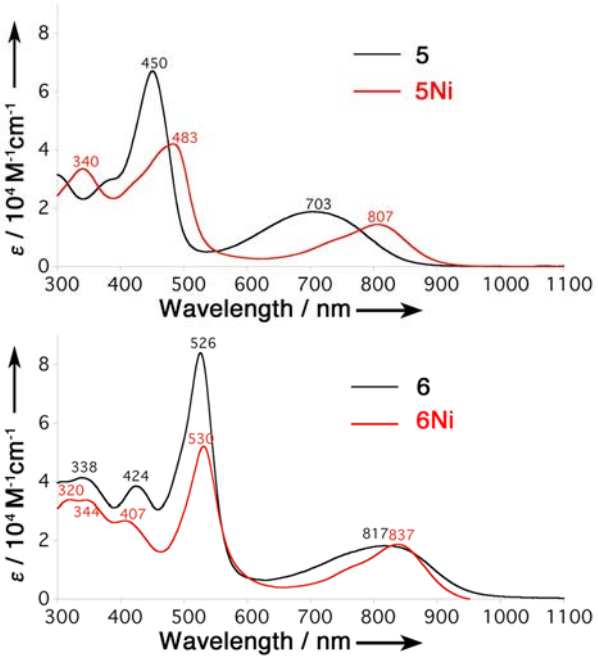


Figure 4. UV/Vis absorption spectra of the expanded diketopyriporphyrins and their Ni complexes in dichloromethane.

In summary, we have synthesized pyripentaphyrin and pyrihexaphyrin which include the tripyrrinone unit with keto-groups neighboring the pyridine unit. The pyridine-expanded porphyrins contain NNNO-type cavities with tripyrrinone type structure. Ni^{II} metalation occurs selectively into the NNNO-type tripyrrinone cavity. From the X-ray structural analysis, We revealed the tripyrrinone ligand with a conjugated structure plays an essential role. It should be noted that they show the same tripyrrinone NNNO coordination system although the entire conformations of **5** and **6** are quite different each other. These data suggest that the Ni^{II} ion prefers the tripyrrinone cavity to other oligopyrrole or pyridine coordination cavities. By designing such tripyrrinone cavity into larger expanded porphyrins, the site-selective coordination of nickel or other metal ions can be promoted even for ligands with other oligopyrrolic coordination sites.

Acknowledgements

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Keywords: Porphyrin • Expanded Porphyrin • NNNO Ligand• Tripyrrinone • Macrocyclic Complex.

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[12] X-ray data for **5**: $(C_{48}H_{22}F_{15}N_5O_2)$•2(ethyl acetate) (Mr = 2500.85), triclinic, space group *P*_1 (No. 2), *a* = 12.0187(2), *b* = 13.5290(3), *c* = 16.7915(3) Å, *α* = 83.478(1)°, *β* = 112.715(4)°, *γ* = 78.564(1)°, *V* = 2500.85(8) Å^3, *Z* = 2, ρ_{calcd} = 1.543 gcm^{-3}, *T* = 93(2) K, R_1 = 0.0994 ($I > 2\sigma(I)$), wR_2 = 0.3206 (all data), GOF = 1.023. CCDC 1953766 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

[13] X-ray data for **6**: 2$(C_{59}H_{24}F_{20}N_6O_2)$•5(1,2-dichloroethane)•0.5(octane) (Mr = 2984.36), monoclinic, space group $P2_1/c$ (No. 14), *a* = 13.7378(3), *b* = 15.7633(4), *c* = 58.8210(13) Å, *β* = 93.066(1)°, *V* = 12719.6(5) Å^3, *Z* = 4, ρ_{calcd} = 1.558 gcm^{-3}, *T* = 93(2) K, R_1 = 0.1379 ($I > 2\sigma(I)$), wR_2 = 0.4361 (all data), GOF = 0.1039. CCDC 1953767 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

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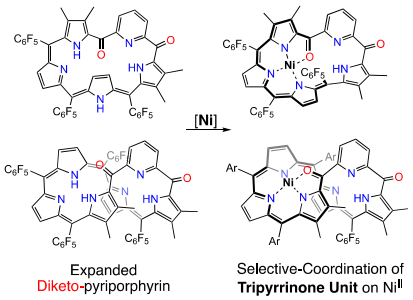
[17] X-ray data for **5Ni**: $C_{48}H_{20}F_{15}N_5O_2Ni \cdot 2$(acetone) (Mr = 1158.54), triclinic, space group *P*_1 (No. 2), *a* = 13.9494(3), *b* = 14.7654(3), *c* = 28.5348(7) Å, *V* = 5017.2(2) Å^3, *Z* = 4, ρ_{calcd} = 1.534 gcm^{-3}, *T* = 93(2) K, R_1 = 0.0904 ($I > 2\sigma(I)$), wR_2 = 0.1987 (all data), GOF = 0.972. CCDC 1953768 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

[18] X-ray data for **6Ni**: 4$(C_{59}H_{22}F_{20}N_6O_2Ni) \cdot$(nonane) (Mr = 5250.16), triclinic, space group *P*_1 (No. 2), *a* = 10.7037(2), *b* = 18.6440(4), *c* = 29.3169(5) Å, *V* = 5403.35(18) Å^3, *Z* = 1, ρ_{calcd} = 1.613 gcm^{-3}, *T* = 93(2) K, R_1 = 0.0585 ($I > 2\sigma(I)$), wR_2 = 0.1748 (all data), GOF = 1.118. CCDC 1953769 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

COMMUNICATION

We report novel expanded porphyrins with a pyridine unit between two *meso*-carbonyl groups. They coordinate to Ni^{II} ions to produce a tripyrrinone-type NNNO coordination structure. Coordination of the tripyrrinone units is highly regioselective in expanded circular pyriporphyrins with many coordination cavities in their structure.



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meso-Diketopyripentaphyrin and Diketopyrihexaphyrin as Macrocyclic Tripyrrinone Ligands for Ni^{II} ions