Synthesis of Box-shaped Pentaporphyrin with Cobalt(II) Porphyrin in the Center; Reversible O_2 Binding in the Box

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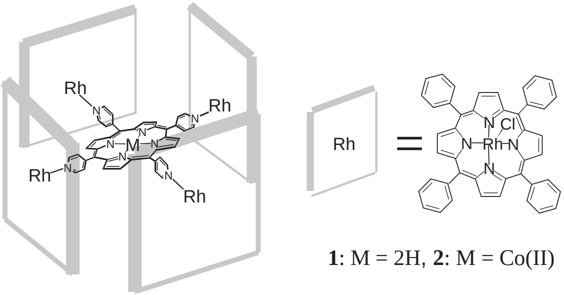
Aiming at construction of robust molecular architectures having an active center surrounded by stable walls, a box-shaped cobalt(II)–rhodium(III) pentaporphyrin [Co(tpyp)][Rh(tpp)Cl]$_4$ (**2**) (tpyp = 5,10,15,20-tetrapyridylporphyrinato dianion, tpp = 5,10,15,20-tetraphenylporphyrinato dianion) was newly synthesized via coordination bonds. The cobalt(II) center of the complex **2** reacts reversibly with O_2 to give a corresponding dioxygen complex of [Co(tpyp)(py)(O_2)][Rh(tpp)Cl]$_4$ (**2**-(py)(O_2)) at low temperatures in dichloromethane-containing pyridine.

Currently, construction of large architectures holding an active center has attracted much attention for develpoping new host–guest chemistry,[1] and site-isolation for effective catalytic activity.[2] From this point of view, porphyrins with coordinating groups and metalloporphyrins should be a promising building units. Planality of the porphyrin units is advantageous for design of large well-defined multidimensional architectures. Moreover, assemblies utilizing coordination bonds have recognized as one of the powerful strategies to construct multidimensional architectures such as cages or capsules,[3,4] helicates,[5] dendritic macromolecules,[6] and porous three-dimensional networks.[7] Actually, combination of porphyrins with coordination groups and metalloporphyrins have given a variety of multiporphyrin architectures including box-shaped pentaporphyrins.[8–10] However, there have been few reports of such large multiporphyrin architectures with active reaction sites for small molecules.[11] The main reason is the unstability of coordination bonds in the reported complexes.

In the present work, by employing rhodium(III) porphyrins, a novel stable box-shaped cobalt(II)–rhodium(III) pentaporphyrin **2** was constructed and characterized (Figure 1). The pentaporphyrin **2** has a cavity (ca. 15 × 15 × 7 Å) in the center, being accessible for small molecules such as dioxygen or dinitrogen. In practice, the pentaporphyrin **2** reacts repeatedly with dioxygen in solution to give a corresponding dioxygen complex.

As a precursor of **2**, the free-base-rhodium(III) pentaporphyrin [H_2tpyp][Rh(tpp)Cl]$_4$ (**1**) was prepared by adding tetrapyridylporphyrin H_2tpyp to the dichloromethane solution of Rh(tpp)Cl and stirring at room temperature, purified by silica-gel column chromatography, and recrystallized from a dichloromethane–pentane solution to give dark black-red fine crystals, followed by characterization.[12] The data of FAB-MAS spectrum and the elemental analysis supported the formation of the expected pentaporphyrin. The UV–vis spectrum of **1** is superposition of each spectrum of constituent porphyrins. The ^{1}H NMR signals of the wall of four rhodium porphyrins are all equivalent. The signals of the pyridyl and β-pyrrole protons of the central free-base pyridylporphyrin showed a large upfield shift, which reflects the coordination of the pyridyl groups to the rhodium porphyrin units.[13] These results are consistent with the box-shaped structure of the pentaporphyrin. To examine the stability of the pentaporphyrin for substitution in dichloromethane, an excess of pyridine (ca. 10% (v/v)) was added. No change in ^{1}H NMR spectrum was observed at least for two days at room temperature. Thus, pyridyl groups coordinated to rhodium(III) porphyrins were not substituted by pyridine, and the rhodium–N(pyridyl) bond is robust enough to keep the pentaporphyrin structure.



1: M = 2H, **2**: M = Co(II)

Figure 1. Box-shaped pentaporphyrins synthesized in this study. The central tetrapyridylporphyrin is surrounded by four walls of rhodium(III) porphyrins.

A cobalt(II) ion was introduced into the central free-base pyridylporphyrin unit in **1** to give **2**. The pentaporphyrin **1** and $CoCl_2 \cdot 6H_2O$ were added to diethylene glycol monomethylether and heated for 2 h at 150 °C. The progress of the reaction was monitored by UV–vis spectral measurements. The solution was cooled to room temperture, followed by the addition of a saturated NaCl aqueous solution. The resulting precipitates were filtered, washed with water, and dried at 100 °C in vacuo. This crude product was purified by silica-gel column chromatography, and recrystallized from a dichloromethane–pentane solution.[14] The inner proton NMR signals of the central pyridylporphyrin observed in **1** disappeared by the introduction of a cobalt(II) ion, and concomitantly appeared the signals of the cobalt pyridylporphyrin unit in an up-field region in comparison with general cobalt(II) monoporphyrins,[15] which indicates that the coordination of the pyridyl groups to the rhodium porphyrin units is retained.

It is well known that cobalt(II) porphyrin forms a corresponding dioxygen adduct in the presence of bases such as pyridine.[16] As mentioned above, our new pentaporphyrin **1** or **2** does not go to pieces in the presence of excess pyridine (see Ref. 10). We examined the reactivity of **2** against molecular oxygen in the presence of pyridine in dichloromethane by ESR and UV–vis spectroscopies. The ESR spectrum of **2**-(py) species formed in 0.5% pyridyne–dichloromethane ([**2**] $\approx 5 \times 10^{-5}$ mol dm^{-3}) showed a characteristic signal of a five-coordinated complex at $g_{\perp} = 2.32$, $g_{\parallel} = 2.04$ ($A_{\parallel}{}^{\mathrm{Co}} = 7.70$ mT, $A_{\parallel}{}^{\mathrm{N}} =$

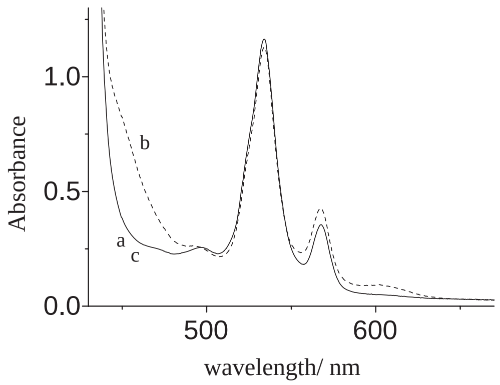
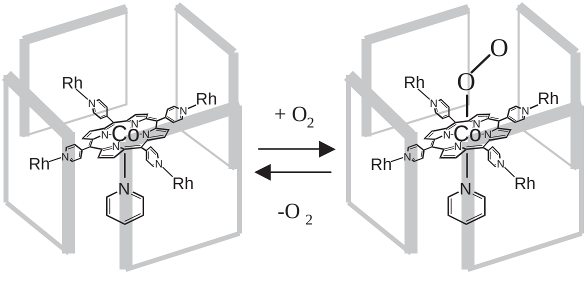


Figure 2. The change in the UV–vis absorption spectra of **2** (1.1×10^{-5} mol dm^{-3}) in 0.3% pyridine–dichloromethane at −70 °C. The spectra were recorded under unaerobic conditions (a; solid line), then under 1 atm O_2 (b; dashed line), and after degassed (c; solid line). Note that, spectra a and c are completely overlapped.

1.80 mT) at −196 °C in vacuo (Figure S1 in Supporting Information).[17] By the introduction of dioxygen to the solution at low temperatures, a corresponding dioxygen complex **2**-(py)(O_2) was formed, i.e., the ESR spectrum of **2**-(py)(O_2) at −196 °C gave a characteristic signal ($g_\perp = 2.01$, $g_\parallel = 2.08$, $A_\perp{}^{Co} = 1.15$ mT, $A_\parallel{}^{Co} = 1.60$ mT) of the six-coordinated cobalt-superoxo species.[17,18] Evacuation with freeze-pump-thaw cycles afforded the original signal of **2**-(py). The oxy/deoxygenation cycles were repeated reversibly. The reversibility was also confirmed by the change in UV–vis spectra. Figure 2 shows that the spectrum of **2**-(py) species (a) changed to that of **2**-(py)(O_2) (b) having a shoulder at around 450 nm in 0.3% (v/v) pyridine–dichloromethane under 1 atmospheric pressure of O_2 at −70 °C.[19] After degassing by freeze-pump-thaw cycles, the initial UV–vis spectrum was completely reproduced (c). No extra chemical reactions were observed, i.e., **2**-(py) can bind molecular oxygen reversibly (Scheme 1). This high reversibility should result from the fact that the cobalt(II) ion of the reaction center was effectively isolated from the cobalt(II) centers of nearby pentaporphyrins by the coordinated bulky rhodium(III) porphyrin walls.

In conclusion, the new robust box-shaped free-base-rhodium(III) pentaporphyrin **1** and the cobalt(II)–rhodium(III) pentaporphyrin **2** were synthesized and characterized. The cobalt(II) complex **2** forms a six-coordinated dioxygen complex at low temperatures in a pyridine–dichloromethane solution. This oxy/deoxygenation reaction in the box is highly reversible. The center of these pentaporphyrins should have a potential applicability as new reaction sites by varying the central metals and porphyrin walls.



Scheme 1. Reversible O_2 binding in the box.

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12 Data for **1** ($C_{216}H_{138}N_{24}Cl_4Rh_4$, MW 3623.0): Anal. Calcd.: C 71.69, H 3.73, N 9.29, Cl 3.91%, Found: C 71.55, H 3.97, N 9.19, Cl 3.70%. FAB-MS: 3623 (m/z^+). UV–vis (CH_2Cl_2), λ_{max}/nm ($\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}): 420 (118), 535 (9.18), 569 (2.47), 646 (0.24). ^{1}H NMR (270 MHz) [δ/ppm in CD_2Cl_2]: 8.97 (32H, s, β Rh), 8.34 (16H, d, *o*-), 8.08, 7.66 (32H, dd, *o*-, *m*-), 7.85 (32H, m, *m*-, *p*-), 6.55 (8H, s, β), 5.38, 1.19 (16H, dd, pyridyl), −4.93 (2H, s, in).

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19 UV–vis data for **2**-(py) in 0.3% (v/v) pyridyne–dichloromethane, λ_{max}/nm: 421, 534, 568; For **2**-(py)(O_2), λ_{max}/nm: 422, 450 (sh), 534, 567. See also Figure S2 in Supporting Information.

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