A Novel Porphyrin Octamer with a Cyclic Tetramer Core

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A novel porphyrin octamer with a ruthenium porphyrin tetrameric core was synthesized and characterized.

For the construction of functional oligomer systems, porphyrin units are very useful in view of their tremendous versatility in electron transfer and photoactivities. In order to prepare these porphyrin oligomers, introduction of pyridyl groups at the meso positions of arylporphyrins[1,2] and also of metal ions such as ruthenium(II) and osmium(II) ions that are relatively inert for substitution, is one of powerful strategies.[3-7]

Introduction of ruthenium ions to the arylporphyrin having one pyridyl group, H_2(4-PyT_3P),[8] gave new cyclic metalloporphyrin tetramers such as [Ru(4-PyT_3P)(CO)]$_4$.[9] The ruthenium(II) porphyrin tetramer exhibits strong interactions between constituent porphyrin subunits in a molecule as observed by UV-vis spectral measurements and cyclic volutammetry (CV), like a case for ruthenium dimer systems.[4] In the presence of a large amount of pyridine the tetrameric complex undergoes decomposition to give a corresponding pyridine coordinated monomer complex. In the presence of an equivalent amount of pyridine, however, the CO ligands directed to the outside of the tetramer core can be substituted by pyridine upon photoirradiation with visible light with preservation of the tetrameric framework to give [Ru(4-PyT_3P)(py)]$_4$.[9] The photosubstitution properties enable us to prepare new oligomers with the tetrameric core.

In the present work, a unique new octamer, [Ru(4-PyT_3P)($H_2$4-PyT_3P)]$_4$, with the cyclic tetramer core was prepared and characterized (Figure 1).

The octamer was prepared by the photosubstitution of arylporphyrins for axial CO ligands in the tetramer core of [Ru(4-PyT_3P)(CO)]$_4$.[10] The IR spectrum (KBr pellet) of the octamer gave no CO stretches which were observed in the parent tetramer at 1964 cm^{-1}. The FAB-MS spectrum of the product gave the parent peak of the octamer at 5658.78 (m/Z^+).

The ^{1}H NMR spectrum obtained for the $C_6D_5CD_3$ solution of the octamer is composed of the signals of the axial porphyrin subunits and the porphyrin tetramer core subunits. The signals were assigned by 2D-NMR measurements and variable temperature methods. The inner protons (NH) of axial porphyrin subunits were observed as a single signal at -2.7 ppm. As observed for the pyridyl groups of the pyridine coordinated tetramer, [Ru(4-PyT_3P)(py)]$_4$,[9] two sets of signals for the 2,6- and 3,5-protons of pyridyl groups in the tetrameric ruthenium porphyrin core appeared around 3 and 6 ppm, respectively, as two double-doublet signals. The signals appeared at 3.25 and 2.62 ppm were ascribed to the 2,6-protons oriented the outer sphere of the tetramer core and to those directed to the center of the core, respectively. With increasing temperature, the double-doublet signals coalesced at around 60 °C to give a single signal, indicating the rotation of the pyridyl ring. On the other hand, the signal of 2,6-pyridyl protons of the axial porphyrin subunits were observed as a single signal at 2.98(d) ppm even at room temperature, and that of 3- and 5-pyridyl protons at 5.35(d) ppm.

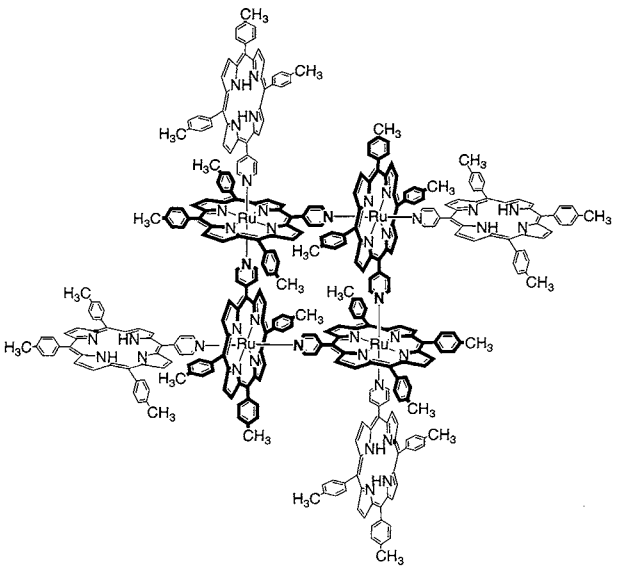

Figure 1. Proposed structure of [Ru(4-PyT_3P)($H_2$4-PyT_3P)]$_4$.

The result indicates that the pyridyl groups of the axial porphyrins are rotating even at room temperature in an NMR relaxation time scale. All these spectroscopic results are consistent with the octameric structure with a tetrameric porphyrin core as shown in Figure 1.

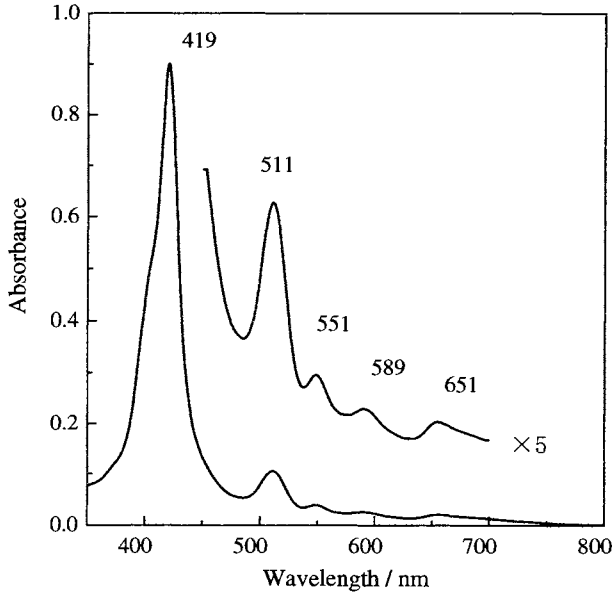

Figure 2. UV-vis spectrum of [Ru(4-PyT_3P)($H_2$4-PyT_3P)]$_4$ in CH_2Cl_2 at 23 °C.

The Soret bands of the octamer are essentially composed of the Soret band of the ruthenium porphyrin core (around 410 nm in CH_2Cl_2, shoulder) and that of axial porphyrin subunits (419 nm) (Figure 2). The absorption at around 410 nm is much weaker than that of free four ruthenium porphyrins as observed in the $[Ru(4\text{-}PyT_3P)(py)]_4$ system,[9] which indicates the presence of the UV-vis spectral interaction between the core constituent porphyrins. The molar absorption coefficient (33.5 x 10^4 $dm^3mol^{-1}cm^{-1}$) of an axial porphyrin subunit at 419 nm is comparable to that of Ru(TTP)($H_2$4-PyT_3P).[3]

Cyclic voltammogram showed the reduction waves of axial porphyrin rings at -1.30 and -1.67 ppm vs. Ag/AgCl in 0.1 mol dm^{-3} $TBA(PF_6)$-CH_2Cl_2 solution at 23 °C and the four-electron broad oxidation wave of Ru(III/II) in the tetramer core porphyrin subunits at around 0.41 V. The broadness of the oxidation wave suggests that the ruthenium ions are oxidized from Ru(II) to Ru(III) stepwise by the intramolecular interactions.[9]

In conclusion, a new octamer with a square cyclic framework was assembled and characterized. This octamer can be used as building blocks in construction of more expanded oligomers with a nanometric scale.

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8 Abbreviations: TPP = 5,10,15,20-tetraphenylporphyrinato dianion; TTP = 5,10,15,20-tetratolylporphyrinato dianion; 4-PyP_3P = 5-pyridyl-10,15,20-triphenylporphyrinato dianion; 4-PyT_3P = 5-pyridyl-10,15,20-tritolylporphyrinato dianion.

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10 Synthesis of the octamer: The parent tetramer $[Ru(4\text{-}PyT_3P)(CO)]_4$ was prepared by the method similar to $[Ru(4\text{-}PyP_3P)(CO)]_4$.[9] $[Ru(4\text{-}PyT_3P)(CO)]_4$ and H_2(4-PyT_3)P were dissolved in 700 ml of toluene. The solution was bubbled with argon and stirred under photoirradiation with visible light (420 - 700 nm) using an medium-pressure mercury lamp until no change in UV-vis spectrum was observed. The solution was evaporated to dryness. The solid material obtained was chromatographed using alumina (neutral, activity 3). The product in methanol was washed on a sintered glass and dried (yield: 61 %).
Elemental Anal (%): Calcd. C, 78.10; H, 4.85; N, 9.90 %. Found: C, 77.15; H, 5.68; N, 8.59 %. UV-vis (CH_2Cl_2) (λmax, ε / 10^4 $dm^3mol^{-1}cm^{-1}$): 410 (shoulder), 419 (134), 511 (14.7), 551 (5.90), 589 (4.13), 651 (3.28). NMR ($C_6D_5CD_3$): -2.72, 2.98(d), 5.35(d), 3.25(d), 2.62(d), 5.97(dd) ppm. CV (CH_2Cl_2): -1.58, -1.25, 0.41, 1.15, 1.47 V (vs. Ag/AgCl, Pt-Pt wire).