Synthesis and Properties of Osmium(II) Porphyrin Oligomers Linked by 3-Pyridylporphyrins

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Introduction

Porphyrin oligomers or polymers assembled as designed in an ordered way have received much interest.[1] Among them, the oligomers constructed using *meso*-pyridyl- (or pyridine ligand-)porphyrins have been studied from various viewpoints. A series of pyridyltriarylporphyrins assembled by Pd(II) or Pt(II) are typical examples.[2]

Recently we reported the synthesis and properties of porphyrin subunit oligomers such as perpendicularly linking or cyclically assembled ruthenium porphyrins[6] and osmium porphyrin oligomers.[7] These porphyrin oligomers are relatively stable even in solution, and the construction of the oligomers with desired molecular structures is quite simple. Furthermore, owing to the facts that two or more porphyrins were closely assembled in a molecule, some dynamic properties of porphyrins were investigated by ^{1}H NMR on osmium porphyrin oligomers containing Os(OEP)(CO) subunits[8] and a series of meso-substituted tetraarylporphyrins, $H_2(4\text{-Py})_nP_{4-n}P$ ($n = 1-4$)[9] as building blocks. Nonsymmetrical porphyrin environment and significant upfield shift of some porphyrin proton signals caused by the ring current of the porphyrin π-electron systems enabled us to observe the tautomerization of internal protons (N−H) of tetraarylporphyrins directly.[7] As a next approach to investigate further the properties of osmium oligomers, we were interested in another type of oligomers prepared by using meso-(3-pyridyl)-substituted porphyrins. Exchange in the axial porphyrin ligand from $H_2(4\text{-Py})_nP_{4-n}P$ to $H_2(3\text{-Py})_nP_{4-n}P$[10] should give a different orientation in the oligomeric structure of porphyrins as shown in Figure 1. We report herein the synthesis and properties of new oligomers, Os(OEP)(CO)[$H_2(3\text{-Py})P_3P$] (**Dimer-Oblique**) and [Os(OEP)(CO)]$_2$[*cis*-$H_2(3\text{-Py})_2P_2P$] (***cis*-Trimer-Oblique**) (Figure 2).

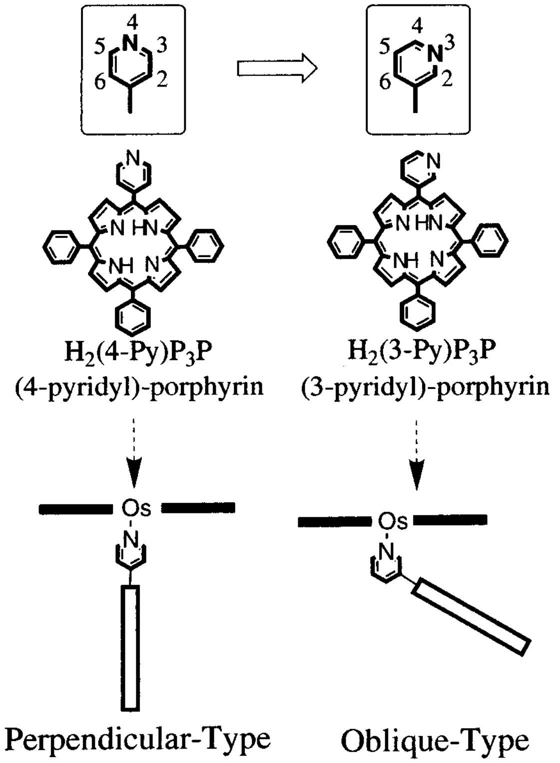
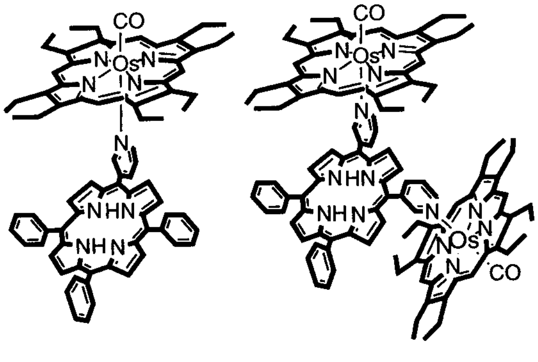


Figure 1. Structural change arisen from the change in the nitrogen atom positions.



Dimer-Oblique ***cis*-Trimer-Oblique**

Figure 2. Oblique-type oligomers.

Experimental Section

The two complexes, Os(OEP)(CO)[$H_2(3\text{-Py})P_3P$] and [Os(OEP)(CO)]$_2$[*cis*-$H_2(3\text{-Py})_2P_2P$] were prepared and recrystallized by the methods similar to perpendicular-type oligomers described previously.[7,11] Elemental analyses were consistent with their chemical formulas. FAB-MS showed the corresponding molecular ion peaks

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(7) Kariya, N.; Imamura, T.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 833.

(8) Abbreviations: H_2OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin; Os(OEP)(CO)(EtOH), carbonyl ethanol octaethylporphyrinato osmium(II); $H_2(3\text{-Py})P_3P$, 5-(3-pyridyl)-10,15,20-triphenylporphyrin; *cis*-$H_2(3\text{-Py})_2P_2P$, 5,10-bis(3-pyridyl)-15,20-diphenylporphyrin; $TBAPF_6$, *n*-tetrabutylammonium hexafluorophosphate.

(9) Fleischer, E. B.; Shachter, A. M. *Inorg. Chem.* **1991**, *30*, 3763.

(10) These derivatives were prepared similarly to $H_2(4\text{-Py})_nP_{4-n}P$ using nicotinaldehyde instead of isonicotinaldehyde, and other derivatives are also known.

(11) As described later, heating the solutions of these oligomers at high temperatures will cause their decompositions. It can be presumed that the reaction temperature affects the yields of oligomers.

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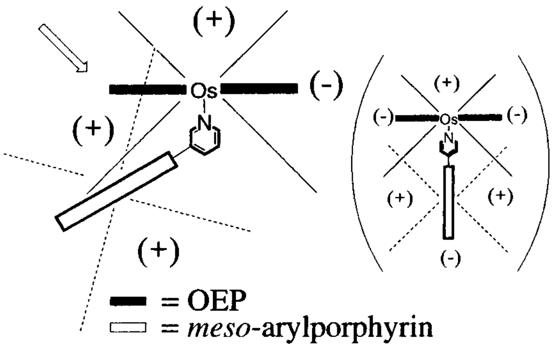

Figure 3. Illustration of the ring current effect experienced by the protons in oligomers. (+) and (−) denote the shielded and deshielded regions, respectively.

clearly at 1367 and 2118 (m/z$^+$) on **Dimer-Oblique** (MW 1366.72) and ***cis*-Trimer-Oblique** (MW 2118.69), respectively. UV−vis spectra of the osmium oligomers in dichloromethane were essentially the sum of those of free Os(OEP)(CO) subunits and H_2(3-Py)P_3P or *cis*-H_2(3-Py)$_2P_2$P. Each of the **Dimer-Oblique** and ***cis*-Trimer-Oblique** showed two Soret bands which could be ascribed to those of constituent porphyrins. IR and ^{1}H NMR spectra also supported the production of the aimed complexes.[12]

Results and Discussion

The structures of these oligomers in solution were verified by ^{1}H NMR measurements. Similarly to perpendicular-type oligomers, large upfield shifts of pyridyl proton peaks on each of the oligomers from those of the parent porphyrins indicated the coordination of pyridyl groups to the osmium ions.[13] Different from perpendicular-type, OEP protons showed an upfield shift ($\Delta\delta$[14] ~ -0.3 ppm).[15] These results reflect the difference in the geometries between the two types of oligomers, i.e., owing to the nonvertical orientation of the OEP planes to those of axial or bridging porphyrins, the OEP protons are positioned in the shielding areas of H_2(3-Py)P_3P or *cis*-H_2(3-Py)$_2P_2$P as shown in Figure 3.

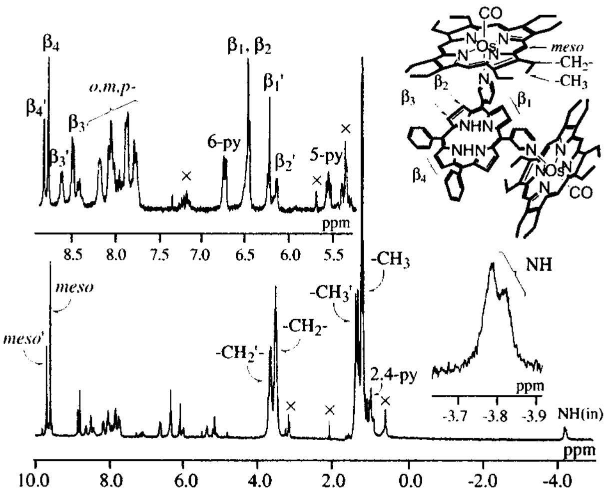

Figure 4. ^{1}H NMR spectrum of ***cis*-Trimer-Oblique** in CD_2Cl_2. "×" denotes solvent and impurity peaks.

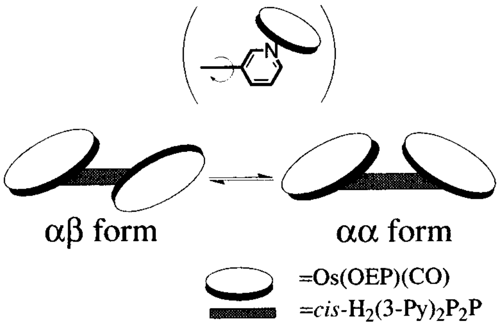

Figure 5. Atropisomers of ***cis*-Trimer-Oblique**.

In ***cis*-Trimer-Oblique**, unlike **Dimer-Oblique**, each peak of OEP protons and of β-pyrrole protons of *cis*-H_2(3-Py)$_2P_2$P distinctly split into two peaks[16] with an intensity ratio of ca. 2:3 in dichloromethane-d_2 (Figure 4), which suggested the presence of the two isomeric forms illustrated in Figure 5. Variable temperature experiments clearly indicated that there is an exchange between the two atropisomers due to the rotation of pyridyl groups. The spectra in the range of OEP (meso) peaks of ***cis*-Trimer-Oblique** at various temperatures are shown in Figure 6. When the solution was heated, two peaks of OEP (meso) were broadened and then coalesced at around 355 K. We failed to evaluate the activation parameters of the atropisomerism accurately because of the decomposition of oligomers at high temperatures, as indicated by distinct arising of the peak at 9.77 ppm of some monomeric OEP (meso). The disassembling was irreversible, since the free monomeric porphyrin peaks remained even after cooling to room temperature. Apparent free energies of activation $\Delta G_c^\ddagger$ were roughly estimated[17] to be ca. 74 kJ mol^{-1} (17.7 kcal mol^{-1}; αα form → $\alpha\beta$ form) and 77 (18.4 kcal mol^{-1}; $\alpha\beta$ form → αα form) kJ mol^{-1} at the coalescence temperature of 355 K (the existence ratio of the αα form to the $\alpha\beta$ form was estimated to be 2:3). The values are almost the same with that of the phenyl ring rotation of Ru(TPP)(CO) (18 kcal mol^{-1})[18] but smaller than that of the rotations ortho-substituted porphyrins ($\sim$130 kJ mol^{-1}).[19,20]

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(12) Data for **Dimer-Oblique**, Os(OEP)(CO)[H_2(3-Py)P_3P] ($C_{80}H_{73}N_9OOs$, MW 1366.72). Anal. Calcd: C, 70.31; H, 5.38; N, 9.22. Found: C, 70.42; H, 5.58; N, 9.37. IR: 1907 cm^{-1} (CO), 3316 cm^{-1} (NH). UV−vis [λ_{max}/nm ($\epsilon/10^4$ M^{-1} cm^{-1}), in CH_2Cl_2]: 371 (7.07), 390 (32.2), 418 (43.8), 513 (2.96), 540 (2.29), 590 (0.73), 646 (0.39). ^{1}H NMR (270 MHz) [δ/ppm in CD_2Cl_2]: 9.64 (4H, s, meso) 3.85 (16H, q (8 Hz), $-CH_2-$), 1.59 (24H, t (8 Hz), −CH3), 8.82 (4H, s, pyrrole β_4,β_3), 8.52 (2H, d (5 Hz), pyrrole β_2), 6.53 (2H, d (5 Hz), pyrrole β1), 8.04−8.27 (6H, m, *o*-,*o′*-), 7.70−7.89 (9H, m, *m*,*p*-), 6.71 (1H, ddd (8, 2, 2 Hz), 6-pyridyl), 5.37 (1H, ddd (8, 6, 2 Hz), 5-pyridyl), 1.24 (1H, m, 2-pyridyl) 1.22 (1H, m, 4-pyridyl), −3.32 (2H, s, in). Cyclic voltammogram [$E_{1/2}$/V vs Ag/AgCl (in 0.1 M $TBAPF_6/CH_2Cl_2$)] −1.49 {H_2(3-Py)$P_3P^{2-/-}$}, −1.16 {H_2(3-Py)$P_3P^{-/0}$}, 0.63 ($Os^{II/III}$), 1.19 ($OEP^{0/+}$), 1.41 ($OEP^{+/2+}$). Data for ***cis*-Trimer-Oblique** [Os(OEP)(CO)]$_2$[*cis*-H_2(3-Py)$_2P_2$P] ($C_{116}H_{116}N_{14}O_2Os_2\cdot 0.5C_6H_5CH_3$, MW 2158.75). Anal. Calcd: C, 66.21; H, 5.60; N, 9.08. Found: C, 66.71; H, 6.09; N, 9.04. IR: 1918 cm^{-1} (CO), 3316 cm^{-1} (NH). UV−vis [λ_{max}/nm, in CH_2Cl_2 ($\epsilon/10^4$ M^{-1} cm^{-1})]: 390 (62.6), 419 (39.4), 514 (4.08), 539 (4.25), 590 (0.732), 647 (0.381). ^{1}H NMR (270 MHz) [δ/ppm in CD_2Cl_2]. Each data means split peaks of atropisomers (see text): 9.67, 9.57 (8H, s, meso) 3.84, 3.71 (32H, m, $-CH_2-$), 1.64, 1.59, 1.47 (48H, m, $-CH_3$), 8.86, 8.81 (2H, s, pyrrole β_4), 8.65, 8.51 (2H, d (5 Hz), pyrrole β_3), 6.43, 6.10 (2H, d (5 Hz), pyrrole β_2), 6.44, 6.19 (2H, s, pyrrole β_1), 7.77−8.48 (10H, m, *o*,*m*,*p*-), 6.71 (2H, m, 6-pyridyl), 5.49 (2H, m, 5-pyridyl), 1.20−1.25 (4H, m, 4-pyridyl, 2-pyridyl), −3.78, −3.83 (2H, in).

(13) The anisotropic effect of porphyrins is often used as a tool to determine the location of certain protons. Janson, T. R.; Katz, J. J. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 4, Chapter 1.

(14) The chemical shift difference $\Delta\delta$ is equal to δ(oligomer) − δ(parent porphyrin monomer).

(15) OEP protons of perpendicular-type oligomers show no upfield shifts (see ref 7).

(16) Considering the shielding effect of OEP ring, OEP's protons in the "αα form" should lie at lower field than those of the "$\alpha\beta$ form". In the αα form, two OEPs position above the *cis*-H_2(3-Py)$_2P_2$P plane (adjacent to each other) and the deshielding by another OEP ring is more effective than in the $\alpha\beta$ form.

(17) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press Inc. Ltd.: London, 1982; Chapters 6 and 7.

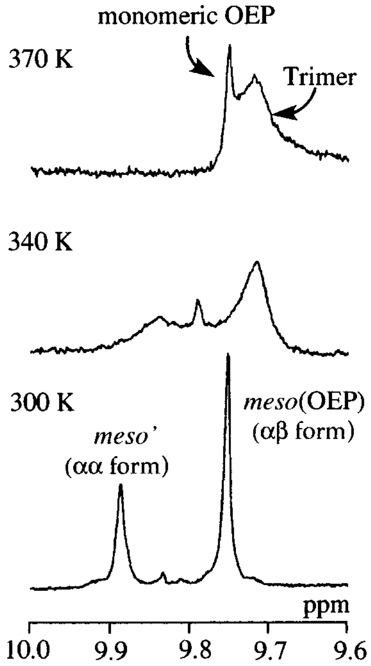

Figure 6. ^{1}H NMR spectra of OEP (meso) protons of ***cis*-Trimer-Oblique** in toluene-d_8 at various temperatures.

The UV−vis spectrum of each oligomer was essentially the sum of those of each component porphyrin like other perpendicular-type oligomers.[5,7] This result indicates that the electronic spectral interaction between the component porphyrin π systems are still difficult even though the geometries of the present oligomers are more favorable than those of perpendicular-type oligomers for the interaction.

Redox behavior was investigated by the cyclic voltammetry for **Dimer-Oblique** in dichloromethane containing 0.1 M $TBAPF_6$. Like the perpendicular-type systems, each component porphyrin in the **Dimer-Oblique** molecule showed independent redox behavior, i.e., the redox potentials and the peak separations of each wave of the osmium and the porphyrin ring redox processes are almost the same as those of monomers except for small potential shifts to the negative direction for the redox wave of the axial porphyrins. The shifts are opposite to those of **Dimer-Perpendicular**, Os(OEP)(CO)[H_2(4-Py)P_3P]. A perpendicular-type dimer shows a positive shift for the redox wave of the axial porphyrin {H_2(4-Py)P_3P}. This was explained in terms of the electron-withdrawing ability of CO group which is at the trans position of the pyridyl group (the first reduction potential of H_2(4-Py)P_3P subunit is −1.05 V vs Ag/AgCl, while that of the free monomer is −1.09 V}.[7] However, **Dimer-Oblique** showed a negative potential shift for axial porphyrin {H_2(3-Py)P_3P} (the first reduction potential of H_2(3-Py)P_3P subunit is −1.16 V). Considering that reduction potentials of monomeric H_2(4-Py)P_3P and H_2(3-Py)P_3P are almost the same (−1.09 V), the difference in the directions of potential shifts between the two dimer systems is thought to be caused essentially by the different positions of nitrogen atoms, H_2(3-Py)P_3P (meta position) and H_2(4-Py)P_3P (para position), on the axial porphyrins, i.e., the binding to Os(OEP)(CO) unit might magnify the difference in natures between these two pyridylporphyrins and the redox potentials are affected in opposite ways.

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