Inorg. Chem. **1997,** *36,* 833−839

Synthesis, Characterization, and Spectral Properties of New Perpendicularly Linked Osmium(II) Porphyrin Oligomers[1]

Nobuko Kariya, Taira Imamura,* and Yoichi Sasaki

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060, Japan

Received July 24, 1996[⊗]

A series of new osmium(II) porphyrin oligomers having tetraarylporphyrins with mixed 4-pyridyl (Py) and phenyl (P) groups, $H_2Py_nP_{4-n}P$, as an axial or a bridging ligand, Os(OEP)(CO)(H_2PyP_3P), **1**, *cis*-[Os(OEP)(CO)]$_2$($H_2Py_2P_2P$), **2**, *trans*-[Os(OEP)(CO)]$_2$($H_2Py_2P_2P$), **3**, [Os(OEP)(CO)]$_3$(H_2Py_3PP), **4**, and [Os(OEP)(CO)]$_4$(H_2TPyP), **5**, were synthesized and characterized by spectroscopic methods. The oligomerizations were confirmed by ^1H NMR. The construction of the oligomers enabled to observe directly the tautomerization of internal N−H protons in the axial porphyrins at low temperatures. The activation energy of the tautomerism, $E_a = 40.5$ kJ mol^{-1}, and the exchanging rate constant, $k = 7200 \pm 100$ s^{-1} at 298 K, were comparable to the values previously reported for various porphyrin monomers. The absorption spectra of these oligomers are essentially superpositions of the spectra of the constituent monomeric porphyrins. The cyclic voltammograms of all the oligomers showed the redox waves of parent porphyrins and the osmium ions, each current reflecting the number of constituents. The peak separations of these Os(II/III) redox waves are nearly the same among the five oligomers. The redox and electronic spectral measurements of the oligomers indicated that there are no distinct interactions between the macrocycles in the ground state electrochemically and visible spectrally.

Introduction

Porphyrin oligomers and polymers are of great interest in relation to molecular materials,[2−4] catalyses,[5−8] or fundamental features in biological systems.[9−15] Among them, porphyrin polymers constructed through coordination bonds, namely those containing porphyrins which can coordinate to metal ions other than the four inner nitrogen atoms, have recently received much attention. In constructing coordination porphyrin polymers, introduction of the pyridyl groups at the meso positions has been the most common strategy. Thus a series of five tetraarylporphyrins with mixed 4-pyridyl and phenyl groups, $H_2Py_nP_{4-n}P$ ($n = 1-4$),[16] are considered as useful building blocks.[17] With these porphyrins, the mutual arrangement of the porphyrins is expected to be perpendicular. The polymers formed from those porphyrins were expected to have interesting structural, electronic, and functional properties which are different from those of the covalently linked porphyrin polymers. A few systems using the 4-pyridyl-substituted porphyrins have been reported. Fleischer et al. revealed the solid and solution state structures of these coordination oligomers,[18,19] and Anderson et al. reported five-porphyrin complexes in attempt to clarify the mechanisms of a positive template in cyclization of linear porphyrin oligomers.[20−25]

Recently, ruthenium(II) porphyrin oligomers such as Ru(OEP)(CO)(H_2PyP_3P), *trans*-[Ru(OEP)(CO)]$_2$($H_2Py_2P_2P$), and Ru(OEP)($H_2Py_2P_2P$)$_2$, which have 4-pyridyl-substituted porphyrins as an axial or a bridging ligand[26,27] and a novel cyclic tetramer,[28] were synthesized. The syntheses suggested the synthetic possibility of porphyrin oligomers which had the same

---

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) This work was presented at the 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 17−22, 1995. Kariya, N.; Imamura, T.; Sasaki, Y. MACR 420. Part of this work was also presented at the 44th Symposium on Coordination Chemistry of Japan, Yokohama, Japan, Nov 21−23, 1994. Kariya, N.; Imamura, T.; Sasaki, Y. Synthesis and Characterization, 2B06.

(2) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.

(3) Segawa, H.; Kunimoto, K.; Susumu, K.; Taniguchi, M.; Shimidzu, T. *J. Am. Chem. Soc.* **1994**, *116*, 11193.

(4) Shimidzu, T.; Segawa, H.; Wu, F.; Nakayama, N. *J. Photochem. Photobiol. A.* **1995**, *92* (1−2), 121.

(5) Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537.

(6) Mackay, L. G.; Wylie, R. S.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1994**, *116*, 3141.

(7) Wylie, R.; Sanders, J. K. M. *Tetrahedron* **1995**, *51*, 513.

(8) Anderson, H.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans 1* **1995**, *18*, 2223.

(9) Susumu, K.; Segawa, H.; Shimidzu, T. *Chem. Lett.* **1995**, 929.

(10) Susumu, K.; Kunimoto, K.; Segawa, H.; Shimidzu, T. *J. Photochem. Photobiol. A.* **1995**, *92* (1−2), 39.

(11) Susumu, K.; Kunimoto, K.; Segawa, H.; Shimidzu, T. *J. Phys. Chem.* **1995**, *99*, 29.

(12) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.

(13) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578.

(14) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618.

(15) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(16) H_2OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin, Os(OEP)(CO)(EtOH) = carbonyl(ethanol)(octaethylporphyrinato)osmium, H_2TPP = 5,10,15,20-tetraphenylporphyrin, H_2PyP_3P = 5-(4-pyridyl)-10,15,20-triphenylporphyrin, *cis*-$H_2Py_2P_2P$ = 5,10-bis(4-pyridyl)-15,20-diphenylporphyrin, *trans*-$H_2Py_2P_2P$ = 5,15-bis(4-pyridyl)-10,20-diphenylporphyrin, H_2Py_3PP = 5,10,15-tris(4-pyridyl)-20-phenylporphyrin, H_2TPyP = 5,10,15,20-tetrakis(4-pyridyl)porphyrin

(17) In addition to the 4-pyridyl groups, 2- and 3-pyridyl derivatives are also known.

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

(19) Shachter, A. M.; Fleischer, E. B.; Haltiwanger, R. C. *J. Chem. Soc., Chem. Commn.* **1988**, 960.

(20) Anderson, H. L.; Hunter, C. A.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commn.* **1989**, 226.

(21) Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469.

(22) Anderson, H.; Anderson, S.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans 1* **1995**, *18*, 2231.

(23) Anderson, S.; Anderson, H.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans I.* **1995**, *18*, 2247.

(24) Anderson, S.; Anderson, H.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans I.* **1995**, *18*, 2255.

(25) Anderson S.; Anderson, H.; Bashall, A.; McPartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1096.

(26) Kimura, A.; Funatsu, K.; Imamura, T.; Kido, H.; Sasaki, Y. *Chem. Lett.* **1995**, 207.

(27) Funatsu, K.; Kimura, A.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.*, in press.

S0020-1669(96)00878-6 CCC: $14.00

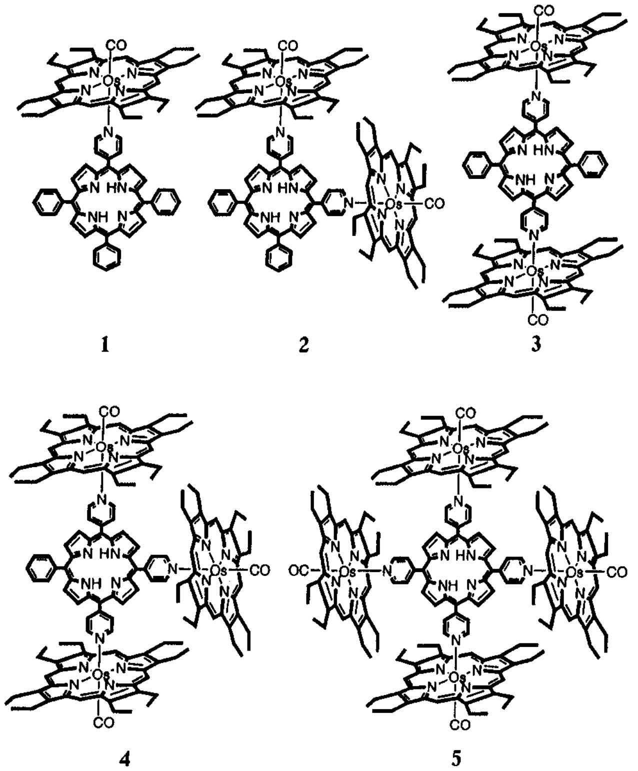

Figure 1. Osmium(II) porphyrin oligomers: Os(OEP)(CO)(H$_2$PyP$_3$P), **1**, *cis*-[Os(OEP)(CO)]$_2$(H$_2$Py$_2$P$_2$P), **2**, *trans*-[Os(OEP)(CO)]$_2$(H$_2$Py$_2$P$_2$P), **3**, [Os(OEP)(CO)]$_3$(H$_2$Py$_3$PP), **4**, and [Os(OEP)(CO)]$_4$(H$_2$TPyP), **5**.

group 8 element, osmium, as ruthenium. In this paper, we report the synthesis and properties of a series of five new osmium(II) porphyrin oligomers[29] using the set of porphyrins with all possible combinations of 4-pyridyl or phenyl groups as substituents, i.e., Os(OEP)(CO)(H$_2$PyP$_3$P), **1**, *cis*-[Os(OEP)(CO)]$_2$(H$_2$Py$_2$P$_2$P), **2**, *trans*-[Os(OEP)(CO)]$_2$(H$_2$Py$_2$P$_2$P), **3**, [Os(OEP)(CO)]$_3$(H$_2$Py$_3$PP), **4**, and [Os(OEP)(CO)]$_4$(H$_2$TPyP), **5**, shown in Figure 1.

Experimental Section

Materials. Parent porphyrins such as Os(OEP)(CO)(EtOH)[30,31] and the mixed pyridine- and phenyl-substituted porphyrins used for axial or bridging ligands, H$_2$PyP$_3$P, *cis*-H$_2$Py$_2$P$_2$P, *trans*-H$_2$Py$_2$P$_2$P, H$_2$Py$_3$PP, and H$_2$TPyP,[18,32] were synthesized according to literature methods. They were purified by silica gel column chromatography. CH$_2$Cl$_2$ used in redox studies was dried over molecular sieves and distilled over CaH$_2$ under Ar just before use. Tetra-*n*-butylammonium hexafluorophosphate ((TBA)PF$_6$) was prepared by mixing aqueous solutions of [(*n*-C$_4$H$_9$)$_4$N]Br and of NH$_4$PF$_6$, and then recrystallized three times from hot ethanol and dried in vacuo. Other solvents and reagents were used as received from Wako Pure Chemicals.

Measurements. UV−vis spectra were measured on a Jasco Ubest-30 spectrophotometer. IR spectra were obtained with a KBr pellet using a Hitachi 270-50 infrared spectrophotometer. FAB-mass spectral measurements and elemental analyses were carried out at the Hokkaido University Machinery Analysis Center. ^{1}H NMR spectra were recorded at room temperature on a JNM-EX400 FT-NMR spectrometer and for variable temperature experiments on a JEOL-EX270 FT-NMR spectrometer. These spectra were referenced against the residual proton resonance of the deuterated solvent (δ(CD$_2$Cl$_2$) 5.30 ppm vs TMS).

Os(OEP)(CO)(H$_2$PyP$_3$P), 1. Os(OEP)(CO)(EtOH) (68 mg, 8.6 × 10^{-2} mmol) and H$_2$PyP$_3$P (46 mg, 7.5 × 10^{-2} mmol) were refluxed in 100 mL of toluene for about 30 min under an Ar atmosphere. The mixture was concentrated to 10−20 mL and chromatographed (SiO$_2$, toluene). The major red band was collected and crystallized from toluene/*n*-hexane (1:10) at room temperature to yield a blue-purple crystalline solid (81 mg, 5.9 × 10^{-2} mmol, 80%). Anal. Calcd for $C_{80}H_{73}N_9OOs$: C, 70.31; H, 5.38; N, 9.22. Found: C, 69.93; H, 5.54; N, 9.44. IR: 1916 (CO), 3318 cm^{-1} (NH). FAB-MS ($C_{80}H_{73}N_9OOs$ = M): *m/z* 1367 (M), 616 (H$_2$PyP$_3$P), 752 [Os(OEP)(CO)], 724 [Os(OEP)]. UV−vis [λ_{max}/nm, in CH$_2$Cl$_2$ ($\epsilon/10^4$ M^{-1} cm^{-1})]: 390 (34.2), 417 (43.3), 513 (2.98), 539 (2.41), 590 (0.701), 646 (0.456). ^{1}H NMR/ppm (CD$_2$Cl$_2$): 9.88 (4H, s, *meso*), 4.05 (16H, q, −CH$_2$−), 1.94 (24H, t, −CH$_3$), 8.70 (2H, d, pyrrole β_4), 8.67 (2H, d, pyrrole β_3), 8.38 (2H, d, pyrrole β_2), 7.16 (2H, d, pyrrole β_1), −3.40 (2H, in), 8.05 (2H, m, *o*′-phenyl), 7.96 (4H, m, *o*-phenyl), 7.65 (9H, m, *m,p*-phenyl), 1.21 (2H, d, 2,6-pyridyl), 5.80 (2H, d, 3,5-pyridyl). The similar synthetic procedure was also applied to the syntheses of **2**, **3**, **4**, and **5**.

***cis*-[Os(OEP)(CO)]$_2$(H$_2$Py$_2$P$_2$P), 2.** Os(OEP)(CO)(EtOH) (80 mg, 10 × 10^{-2} mmol) and *cis*-H$_2$Py$_2$P$_2$P (32 mg, 5.2 × 10^{-2} mmol) gave a purple solid (39 mg, 2.0 × 10^{-2} mmol, 40%). Anal. Calcd for $C_{116}H_{116}N_{14}O_2Os_2$: C, 65.76; H, 5.52; N, 9.26. Found: C, 65.77; H, 5.42; N, 9.09. IR: 1916 (CO), 3319 cm^{-1} (NH). FAB-MS ($C_{116}H_{116}N_{14}O_2Os_2$ = M): *m/z* 2119 (M), 1367 [M − Os(OEP)(CO)], 1340 [Os(OEP)(H$_2$Py$_2$P$_2$P)], 618 (H$_2$Py$_2$P$_2$P), 752 [Os(OEP)(CO)]. UV−vis [λ_{max}/nm, in CH$_2$Cl$_2$ ($\epsilon/10^4$ M^{-1} cm^{-1})]: 390 (63.2), 417 (38.6), 512 (4.06), 538 (4.39), 588 (0.819), 646 (0.435). ^{1}H NMR/ppm (CD$_2$Cl$_2$): 9.86 (8H, s, *meso*), 4.06 (32H, q, −CH$_2$−), 1.95 (48H, t, −CH$_3$), 8.52 (2H, s, pyrrole β_4), 8.23 (2H, d, pyrrole β_3), 6.98 (2H, d, pyrrole β_2), 6.68 (2H, s, pyrrole β_1), −3.96 (2H, in), 7.79 (4H, m, *o*-phenyl), 7.65, 7.56 (6H, m, *m,p*-phenyl), 1.12 (4H, d, 2,6-pyridyl), 5.55 (4H, d, 3,5-pyridyl)

***trans*-[Os(OEP)(CO)]$_2$(H$_2$Py$_2$P$_2$P), 3.** Os(OEP)(CO)(EtOH) (78 mg, 9.8 × 10^{-2} mmol) and *trans*-H$_2$Py$_2$P$_2$P (31 mg, 5.0 × 10^{-2} mmol) gave a crystalline purple solid (39 mg, 2.0 × 10^{-2} mmol, 40%). Anal. Calcd for $C_{116}H_{116}N_{14}O_2Os_2$: C, 65.76; H, 5.52; N, 9.26. Found: C, 65.98; H, 5.39; N, 9.32. IR: 1916 (CO), 3318 cm^{-1} (NH). FAB-MS ($C_{116}H_{116}N_{14}O_2Os_2$ = M): *m/z* 2120 (M), 1367 [M − Os(OEP)(CO)], 1340 [Os(OEP)(H$_2$Py$_2$P$_2$P)], 616 (H$_2$Py$_2$P$_2$P), 752 [Os(OEP)(CO)]. UV−vis [λ_{max}/nm, in CH$_2$Cl$_2$ ($\epsilon/10^4$ M^{-1} cm^{-1})]: 390 (58.7), 417 (49.8), 512 (4.18), 538 (4.06), 589 (0.901), 646 (0.624). ^{1}H NMR/ppm (CD$_2$Cl$_2$): 9.82 (8H, s, *meso*), 3.99 (32H, q, −CH$_2$−), 1.89 (48H, t, −CH$_3$), 8.20 (4H, d, pyrrole β_2), 7.01 (4H, d, pyrrole β_1), −3.97 (2H, in), 7.70 (4H, m, *o*-phenyl), 7.66, 7.55 (6H, m, *m,p*-phenyl), 1.14 (4H, d, 2,6-pyridyl), 5.65 (4H, d, 3,5-pyridyl)

[Os(OEP)(CO)]$_3$(H$_2$Py$_3$PP), 4. Os(OEP)(CO)(EtOH) (90 mg, 12 × 10^{-2} mmol) and H$_2$Py$_3$PP (25 mg, 4.1 × 10^{-2} mmol) gave a red purple solid (28 mg, 0.99 × 10^{-2} mmol, 24%). Anal. Calcd for $C_{152}H_{159}N_{19}O_3Os_3$: C, 63.60; H, 5.58; N, 9.27. Found: C, 63.27; H, 5.53; N, 9.13. IR: 1917 cm^{-1} (CO). FAB-MS: *m/z* 1367 [Os(OEP)(CO)(H$_2$Py$_3$PP)], 619 (H$_2$Py$_3$PP), 753 [Os(OEP)(CO)]. UV−vis [λ_{max}/nm, in CH$_2$Cl$_2$ ($\epsilon/10^4$ M^{-1} cm^{-1})]: 390 (87.4), 417 (35.7), 512 (5.08), 538 (6.08), 590 (1.00), 647 (0.502). ^{1}H NMR/ppm (CD$_2$Cl$_2$): 9.84 (4H, s, *meso*), 9.79 (8H, s, *meso*′), 4.06 (16H, q, −CH$_2$−), 3.99 (32H, q, −CH$_2$′−), 1.94 (24H, t, −CH$_3$), 1.88 (48H, t, −CH$_3$′), 8.05 (2H, d, pyrrole β_4), 6.84 (2H, d, pyrrole β_3), 6.51 (4H, m, pyrrole β_2, β_1), −4.59 (2H, in), 7.53, 7.46 (5H, m, *o,m,p*-phenyl), 1.03 (6H, d, 2,6-pyridyl), 5.39 (6H, d, 3,5-pyridyl)

[Os(OEP)(CO)]$_4$(H$_2$TPyP), 5. Os(OEP)(CO)(EtOH) (103 mg, 16 × 10^{-2} mmol) and H$_2$TPyP (24 mg, 3.9 × 10^{-2} mmol) gave a dark red purple solid (32 mg, 0.89 × 10^{-2} mmol, 21%). Anal Calcd for $C_{188}H_{202}N_{24}O_4Os_4$: C, 62.33; H, 5.62; N, 9.28. Found: C, 61.93; H, 5.66; N, 9.16. IR: 1919 cm^{-1} (CO). FAB-MS: *m/z* 1370 [Os(OEP)(CO)(H$_2$TPyP)], 619 (H$_2$TPyP), 752 [Os(OEP)(CO)]. UV−vis [λ_{max}/nm, in CH$_2$Cl$_2$ ($\epsilon/10^4$ M^{-1} cm^{-1})]: 390 (115), 418 (34.0), 510 (6.09), 538 (7.72), 589 (1.16), 649 (0.519). ^{1}H NMR/ppm (CD$_2$Cl$_2$): 9.77 (16H, s, *meso*), 4.01 (64H, q, −CH$_2$−), 1.88 (72H, t, −CH$_3$), 6.35 (8H, s, pyrrole β), −5.11 (2H, in), 0.93 (8H, d, 2,6-pyridyl), 5.14 (8H, d, 3,5-pyridyl)

---

[28] Funatsu, K.; Kimura, A.; Imamura, T.; Sasaki, Y. *Chem. Lett.* **1995**, 765.

[29] During the preparation of this manuscript, the same series of (except for type of **4**) vertically linked ruthenium(II) porphyrins was reported: Alessio, E.; Macchi, M.; Heath, S.; Marzilli, L. G. *J. Chem. Soc., Chem. Commun.* **1996**, 1411. The spectroscopic results of the compound reported herein are very similar to those compounds.

[30] Buchler, J. W.; Rohbock, K. *J. Organomet. Chem.* **1974**, *65*, 223.

[31] Che, C.-M.; Poon, C.-K.; Chung, W.-C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277.

[32] Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, *48*, 4251.

Table 1. UV−Vis Data for Porphyrin Oligomers and Monomers

compound	solvent	λ_{max}/nm (ϵ/10^4 M^{-1} cm^{-1})					
		Soret (B_2)	Soret (B_1)	Q band			
Os(OEP)(CO)(EtOH)	$CHCl_3$[a]	391(32.4)		510(1.29)	541(2.34)		
Os(OEP)(CO)(Py)	CH_2Cl_2	394(30.2)		510(1.29)	540(2.04)		
H_2TPP	CH_2Cl_2[b]		416(49)	520(1.6)	549(0.8)	590(0.6)	644(0.4)
H_2TPyP	$CHCl_3$[c]		417(42.5)	513(1.96)	547(0.54)	588(0.59)	643(0.17)
H_2PyP_3P	$CHCl_3$[d]		417(45.7)	512(2.04)	547(0.74)	567(0.60)	643(0.36)
H_2PyP_3P[e]	CH_2Cl_2		416(47.4)	514(1.91)	548(0.73)	589(0.56)	645(0.36)
[Os(OEP)(CO)](H_2PyP_3P), **1**	CH_2Cl_2	390(34.2)	417(43.3)	513(2.98)	539(2.41)	590(0.701)	646(0.456)
cis-[Os(OEP)(CO)]$_2$($H_2Py_2P_2P$), **2**	CH_2Cl_2	390(63.2)	417(38.6)	512(4.06)	538(4.39)	588(0.819)	646(0.435)
trans-[Os(OEP)(CO)]$_2$($H_2Py_2P_2P$), **3**	CH_2Cl_2	390(58.7)	417(39.8)	512(4.18)	538(4.06)	589(0.901)	646(0.624)
[Os(OEP)(CO)]$_3$(H_2Py_3PP), **4**	CH_2Cl_2	390(87.4)	417(35.7)	512(5.08)	538(6.08)	590(1.00)	647(0.502)
[Os(OEP)(CO)]$_4$(H_2TPyP), **5**	CH_2Cl_2	390(115)	418(34.0)	510(6.09)	538(7.72)	589(1.16)	649(0.519)

[a] Buchler, J. W.; Rohbock, K. *J. Organomet. Chem.* **1974**, *65*, 223. [b] Rousseau, K.; Dolphin, D. *Tetrahedron Letters* **1974**, *48*, 4251. [c] Fleischer, E. B. *Inorg. Chem.* **1962**, *1*, 493. [d] Williams, G. N.; Williams, R. F. X.; Lewis, A.; Hambright, P. *J. Inorg. Nucl. Chem.* **1979**, *41*, 41. Molar absorptivities were calculated from original values in log(ϵ). [e] Five mixed substituted porphyrins, H_2PyP_3P, *cis*-$H_2Py_2P_2P$, *trans*-$H_2Py_2P_2P$, H_2Py_3PP, and H_2TPyP, showed almost the same absorptions.

Results and Discussion

The series of osmium(II) porphyrin oligomers was prepared from the reaction of the Os(OEP)(CO)(EtOH) with 4-pyridyl-substituted porphyrins ($H_2Py_nP_{4-n}P$; $n = 1-4$), with the 1:n molar ratio of $H_2Py_nP_{4-n}P$ to Os(OEP)(CO)(EtOH) in toluene at reflux temperature. The oligomers were characterized as follows.

IR Spectra. All oligomers showed characteristic CO stretches in the region 1916−1919 cm^{-1}. There is no distinct trend of ν(CO) among the oligomers. The wavenumbers are higher by *ca.* 10 cm^{-1} than those of the corresponding porphyrin monomers such as Os(OEP)(CO)(EtOH) (1899 cm^{-1}) and Os(OEP)(CO)(Py) (1901 cm^{-1}).[33] A similar trend of the CO stretching was also observed in the ruthenium oligomer systems.[26,27] The N−H stretches of the axial or bridging porphyrins on **1**, **2**, and **3** were observed at 3318, 3319, and 3318 cm^{-1}, respectively. These values were almost the same as those of free tetraarylporphyrins, indicating little effect of Os(OEP) moieties on N−H vibrations.

Visible Spectra. All compounds exhibited six distinct absorption maxima in the visible region. The spectral profiles showed no fundamental differences among these oligomers except for the relative intensities, which reflect the ratio of constituting porphyrins. The numerical data of the spectra are summarized in Table 1. The typical spectra as represented by **1** and **5** are shown in Figure 2. The absorption bands around 420 (B_1) and 390 nm (B_2) were assigned to the Soret bands of mixed 4-pyridyl- and phenyl-substituted porphyrin (H_2PyP_3P − H_2TPyP) and Os(OEP)(CO) parts, respectively. The ratio of molar absorptivities of two Soret bands, B_2/B_1, roughly reflected the compositions of oligomers. For instance, B_2/B_1 for **1** and **5** are 0.79 ($=34.2 \times 10^4/43.3 \times 10^4$) and 3.38 ($=115 \times 10^4/34.0 \times 10^4$), respectively, and the value for **5** is about 4 times as much as the value for **1**.

Two absorption maxima around 600 and 650 nm should be assigned to the Q bands of axial or bridging porphyrins. They also located at almost the same wavelengths with similar molar absorptivities to those of Q bands observed for free tetraarylporphyrins. The results revealed that the absorption spectra of these systems are approximately superpositions of the spectra of the constituent monomeric porphyrins, and there are no interactions visible spectrally between the porphyrin subunits in a molecule. These properties are quite different from some covalently linked oligomers, in which highly perturbed optical spectra are observed.[34−41] The absence of interactions are not surprising given that the structures of the oligomers linked perpendicularly prevent both extension and overlapping of aromatic π-systems.

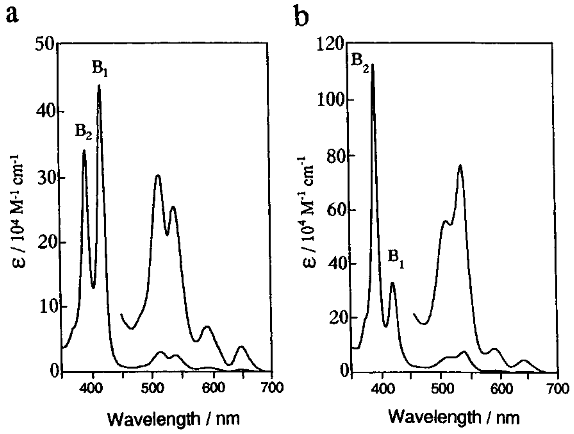

Figure 2. UV−visible spectra of (a) Os(OEP)(CO)(H_2PyP_3P), **1**, and (b) [Os(OEP)(CO)]$_4$(H_2TPyP), **5**, in dichloromethane at room temperature.

^{1}H NMR Spectra. The oligomers showed sharp ^{1}H NMR signals, as shown in Figure 3, suggesting these are diamagnetic oligomers. There were essentially no distinct peaks for the free monomer in each oligomer, even in the variable temperature measurements; i.e., the equilibrium of coordination lies so far to the oligomers.

The signals are composed of the parts of OEP and axial or bridging tetraarylporphyrins. The OEP parts appeared at almost the same chemical shifts of starting material monomer, Os(OEP)(CO)(EtOH). The inner proton (N−H) signals of 4-pyridyl-substituted porphyrins were located at the most highest field region of −3 to −4.5 ppm. The integral intensity ratios of the signals of the OEP rings and of N−H confirmed the compositions of the oligomers **1**−**5**.

---

(33) Buchler, J. W.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *136*, 745.

(34) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972.

(35) Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron* **1992**, *48*, 8781.

(36) Guilard, R.; Lopez, M. A.; Tabard, A.; Richard, P.; Lecomte, C.; Brandes, S.; Hutchison, J. E.; Collman, J. P. *J. Am. Chem. Soc.* **1992,** *114*, 9877.

(37) Leighton, P.; Cowan, J. A.; Abraham, R. J.; Sanders, J. K. M. *J. Org. Chem.* **1988**, *53*, 733.

(38) Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1988**, *110*, 4454.

(39) Sessler, J. L.; Hugdahl, J.; Johnson, M. R. *J. Org. Chem.* **1986**, *51*, 2838.

(40) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y.; Creager, S. E. *J. Am. Chem. Soc.* **1988**, *110*, 3659.

(41) Kadish, K. M.; Vancaemelbecke, E.; Dsouza, F.; Medforth, C. J.; Smith, K. M.; Tabard, A.; Guilard, R. *Inorg. Chem.* **1995**, *34*, 2984.

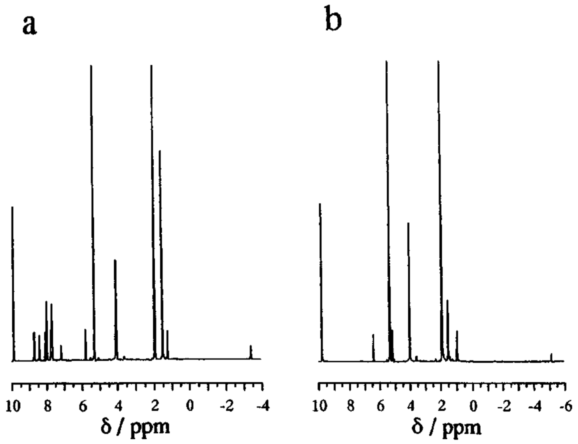

Figure 3. ^{1}H NMR spectra of (a) Os(OEP)(CO)(H_2PyP_3P), **1**, and (b) $[Os(OEP)(CO)]_4(H_2TPyP)$, **5**, in dichloromethane-d_2 at room temperature.

Table 2. Ring Current Shifts of Oligomers[a]

	pyridyl	N−H	pyrrole	phenyl
1	2,6-: −7.48 3,5-: −2.22	−0.52	β_4: −0.15 β_3: −0.18 β_2: −0.47 β_1: −1.69	*o′*-: −0.15 *o*-: −0.24 *m,p*-: −0.13
2	2,6-: −7.89 3,5-: −2.65	−1.06	β_4: −0.35 β_3: −0.64 β_2: −1.54 β_1: −1.84	*o*-: −0.41 *m,p*-: −0.18 −0.13
3	2,6-: −7.88 3,5-: −2.57	−1.07	β_2: −0.72 β_1: −1.81	*o*-: −0.52 *m,p*-: −0.23 −0.12
4	2,6-: −8.00 3,5-: −2.82	−1.62	β_4: −0.83 β_3: −2.04 β_2, β_1: −2.37	*o*-: −0.68 *m,p*-: −0.33 −0.21
5	2,6-: −8.09 3,5-: −3.02	−2.13	β: −2.54	

[a] $\Delta\delta = \delta$(oligomer) − δ(parent tetraarylporphyrin)/ppm.

Ring currents in porphyrins cause changes in chemical shifts of the protons located near the porphyrin plane.[18,37,42−45] The protons in each (4-pyridyl)porphyrin was surely upfield shifted from its parent porphyrin because of the OEP ring current.[26,27] In particular, the extent of upfield shifts of the 2,6- and 3,5-pyridyl protons in the axial porphyrins were large, while the phenyl protons showed almost no shift. In the dimer of **1**, the ring current shift, $\Delta\delta = \delta$(oligomer) − δ(parent porphyrin), of 2,6-pyridyl protons was −7.48 ppm and that of *m,p*-phenyl protons was −0.13 ppm (Table 2). Thus, it is reasonable to consider that the 2,6-pyridyl protons are located at the nearest positions to the OEP ring core of Os(OEP)(CO), which implies the coordination of the pyridyl groups of the (4-pyridyl)-porphyrins to Os ions.[18,21,23,25−27,46] The spectral features, namely the equivalence of 2- and 6-pyridyl protons as well as 3- and 5-protons, indicate that the axial or bridging tetraarylporphyrins are positioned vertically to the OEP planes at least on average on a ^{1}H NMR time scale.

The values of the chemical shift differences from those of corresponding free ligands, $\Delta\delta$, increased with increment number of the OEP rings. The $\Delta\delta$ was the most sensitive to the number for N−H protons as shown in Figure 4, i.e., −0.52 for **1** and −2.13 ppm for **5**, that is about 4 times of **1**. However, the difference in $\Delta\delta$ of 2,6-pyridyl protons was very small, i.e., the values of $\Delta\delta$ were −7.48 and −8.09 ppm for **1** and **5**, respectively. This result can be simply explained by the locations of the protons. 2,6-Pyridyl protons are located at the position nearest to one of the OEPs which gives the largest high-field shift, but outside of the effective shielding area of other OEPs. In contrast, N−H protons are located at the same distances from each OEP ring and are equally affected by each OEP.

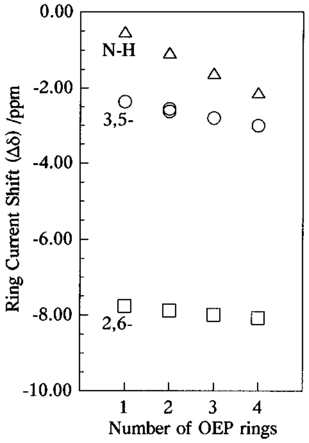

Figure 4. Plots of ring current shift {$\Delta\delta = \delta$(oligomer) − δ(parent porphyrin)} vs the number of OEP rings in one molecule. The presence of two data points at number 2 is due to the oligomers, *cis*-$[Os(OEP)(CO)]_2(H_2Py_2P_2P)$, **2**, and *trans*-$[Os(OEP)(CO)]_2(H_2Py_2P_2P)$, **3**.

Observation of Porphyrin Tautomerism. As discussed in the previous section, the OEP rings in these oligomers induced large ring current shifts on the protons of axial or bridging porphyrins depending on the distances between the protons and the OEP ring centers. Therefore in principle, one can observe the two kinds of internal proton (N−H) signals of the axial tetraarylporphyrins if the rate of proton exchange over four nitrogens is sufficiently slow on the ^{1}H NMR time scale. In other porphyrins containing no effective shielding or deshielding systems (aromatics, or β-substituents) it may be impossible to discriminate between them by ^{1}H NMR spectral measurements since either all the nitrogen sites are equivalent or the chemical shift difference is too small. In such cases various alternative methods were required to study the N−H exchange system, such as observation of pyrrole β-protons,[47−49] peripheral modification,[50−52] ^{15}N labeling,[49,53−56] or other multinuclear NMR measurements.[56]

Typical internal proton signals for the systems of **1** and **2** are shown in Figure 5. In both systems, the signals of N−H

---

(42) Janson, T. R.; Katz, J. J. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. IV, p 9.
(43) Skog, K.; Wennerström, O. *Tetrahedron* **1994**, *50*, 8227.
(44) Abraham, R. J.; Bedford, G. R.; Neillie, D. M.; Wright, B. *Org. Magn. Reson.* **1980**, *14*, 418.
(45) Cross, K. J.; Crossley, M. J. *Aust. J. Chem.* **1992**, *45*, 991.
(46) Collman, J. P.; Little, W. A.; Torrance, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4581.
(47) Storm, C. B.; Teklu, Y. *J. Am. Chem. Soc.* **1972**, *94*, 1745.
(48) Storm, C. B.; Teklu, Y.; Sokoloski, E. A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 631.
(49) Hennig, J.; Limbach, H. H. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 752.
(50) Crossley, M. J.; Field, L. D.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* **1987**, *109*, 2335.
(51) Crossley, M. J.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* **1986**, *108*, 3608.
(52) Crossley, M. J.; Harding, M. M.; Sternhell, S. *J. Org. Chem.* **1992**, *57*, 1833.
(53) Schlabach, M.; Wehrle, B.; Limbach, H. H.; Bunnenberg, E.; Knierzinger, A.; Shu, A. Y. L.; Tolf, B.; Djerassi, C. *J. Am. Chem. Soc.* **1986**, *108*, 3856.
(54) Gust, D.; Roberts, J. D. *J. Am Chem. Soc.* **1977**, *99*, 3637.
(55) Yeh, H. J. C.; Sato, M.; Morishima, I. *J. Magn. Reson.* **1977**, *26*, 365.
(56) Schlabach, M.; Wehrle, B.; Rumpel, H.; Braun, J.; Scherer, G.; Limbach, H. H. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 821.

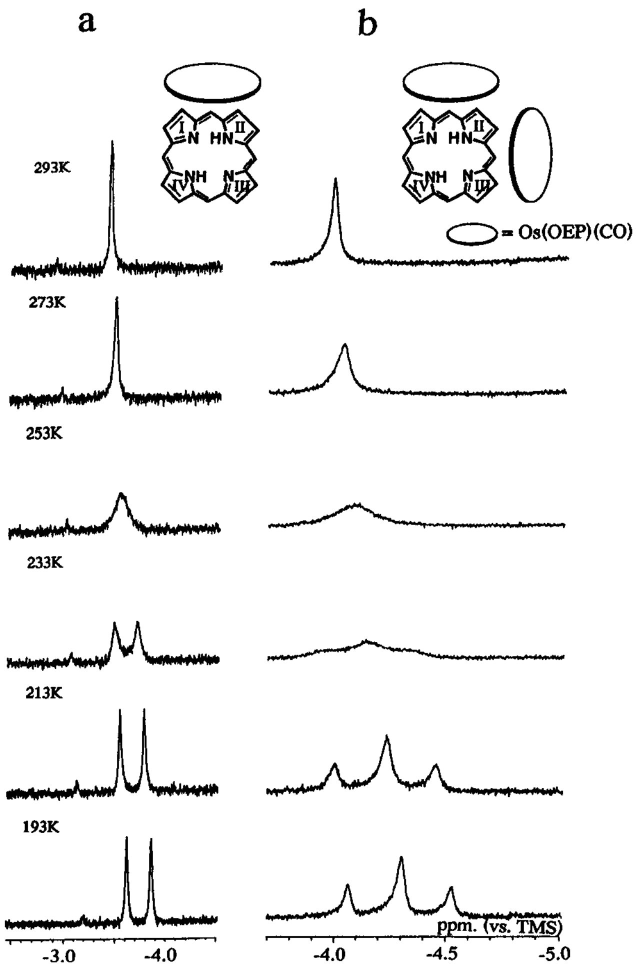

Figure 5. ${}^1H$ NMR spectra of the N−H protons at various temperatures for (a) Os(OEP)(CO)(H_2PyP_3P), **1**, and (b) *cis*-[Os(OEP)(CO)]$_2$-($H_2Py_2P_2P$), **2**, in toluene-d_8. The minor signal at ∼−3.2 ppm in **a** (193 K) is the N−H proton of free H_2PyP_3P, which arose from the decomposition of the oligomer by a long time measurement process.

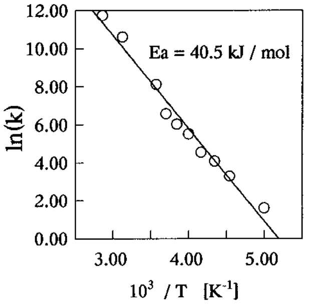

Figure 6. Arrhenius diagram for the tautomerism of Os(OEP)(CO)-(H_2PyP_3P), **1**.

protons were broadened and split into two or three signals as the temperatures were lowered. The signal in higher field for **1** was assigned to the N−H on the pyrrole ring of ring I or II and the other to that on ring III or IV shown in the upper parts of Figure 5. The exchange rate constant, k, was evaluated by adapting the theoretical line shapes[57] to the digitized experimental spectra. A plot of ln(k) vs 1/T afforded a nearly straight line over the range from 220 to 320 K, as shown in Figure 6. The activation energy, E_a, obtained as 40.5 kJ mol^{-1} was comparable to the values of general porphyrin monomers.[49,56] The k at 298 K is evaluated to be 7200 ± 100 s^{-1}.

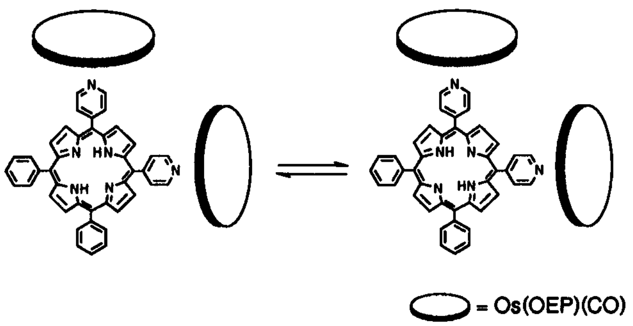

Figure 7. Tautomer of *cis*-[Os(OEP)(CO)]$_2$($H_2Py_2P_2P$), **2**.

The N−H protons of **2** showed three peaks with 1:2:1 intensities at low temperatures (Figure 5b). Considering the effect of OEP ring current, the signals at ∼−4.52, −4.30, and ∼−4.05 ppm at 193 K were assigned to the N−H protons bound to rings II, I or III, and IV, respectively. Thus two tautomers of **2** shown in Figure 7 were detected through N−H proton signals at low temperatures. The integral intensities of the signals showed that the two isomers exist in the ratio of almost 1:1, suggesting that the equilibrium constant of the tautomerism is unity. Although the free porphyrin itself, H_2PyP_3P, *cis*-$H_2Py_2P_2P$, or H_2Py_3PP, has also two or three kinds of magnetic environments for N−H due to the unsymmetrical positioning of pyridyl groups, the obtained spectra showed only one resonance even at 193 K. This must result from the similarities of magnetic environments of each sites of the free porphyrins.

The N−H signals of **3** and **5** showed no broadening and splitting in the temperature range 190−310 K, as expected from the fact that these oligomers and their bridging porphyrins themselves have D_{2h} and D_{4h} symmetries when inner protons are ignored and that two pairs of inner nitrogen sites are chemically equivalent. The tautomerization of these oligomers, **3** and **5**, was observed on their pyrrole β-proton resonances as reported in the previous papers for general porphyrin monomers.[47−49] In contrast to the small change of the phenyl or pyridyl multiplets over the temperature range of 190−310 K, each pyrrole β-proton of the oligomers including **3** and **5**, splits into two peaks due to the slow down of the proton migrations at low temperatures. The pyrrole β-proton signals of **1** are shown in Figure 8. The signals in the lower field were assigned to the β-proton of pyrrole rings with protonated N and the others were assigned to those on the deprotonated pyrrole rings. The peaks at lower field were slightly broader, which indicates the long range coupling to the N−H protons.[47,48]

Redox Properties of Oligomers. Redox properties of five oligomers in dichloromethane were studied by cyclic voltammetry (Figure 9). The data are summarized in Table 3.

The voltammograms of all the oligomers showed very simple redox waves which were ascribed to constituent porphyrin rings and osmium ions. The reversible waves of Os(II/III) were observed around 0.6 V (vs Ag/AgCl). The values were nearly the same with that of Os(OEP)(CO)(Py).[58] Each current reflected the number of Os(OEP)(CO) parts constructing the oligomers, i.e., the relative current value of Os(II/III) to the that of axial or bridging porphyrin for **5** was 4 times that for **1**. The peak separations of these Os(II/III) redox waves (cathodic-to-anodic peak separation: $\Delta(E_{pa} - E_{pc}) \approx 80$ mV) are nearly the same among the five oligomers. These results indicate that each Os(II/III) wave corresponds to two one-electron (1e) redox processes in the case of **2** and **3**, three 1e in **4**, and four 1e in **5**. It is clear that there are no distinct electrochemical

---

(57) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press Inc. Ltd.: London, 1982; p 93.

(58) Brown, G. M.; Hopf, F. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 5385.

Table 3. Half-Wave Potentials of Oligomers (CH_2Cl_2, 0.1 M $(TBA)PF_6$)

	$E_{1/2}$ in V vs Ag/AgCl ($\Delta E_p = E_{pa} - E_{pc}$)		
compound	ring redn	metal	ring oxidn
Os(OEP)(CO)(Py)		0.61 (70)	1.40 (80)
H_2TPP^a			1.00, 1.20
H_2TPP^b	−1.05, −1.47		
H_2PyP_3P	−1.09 (80), −1.41 (70)		1.15 (70)
1	−1.05 (70), −1.33 (70)	0.63 (70)	1.23 (70), 1.39 (60), 1.48 (E_{pa})
2	−0.97 (70), −1.24 (80)	0.66 (80)	1.38 (80), 1.56 (E_{pa})
3	−0.99 (70), −1.24 (120)	0.64 (60)	1.39 (80), 1.49 (E_{pa})
4	−0.91 (80), −1.32 (E_{pc})	0.65 (60)	1.38 (100)
5	−0.82 (140), −1.32 (E_{pc})	0.66 (60)	1.37 (100), 1.64 (E_{pa})

[a] $(TBA)PF_6$ in benzonitrile in V vs SCE: Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982. [b] Polarographic results: TPAP in DMSO in V vs SCE: Felton, R. H.; Linschitz, H. *J. Am. Chem. Soc.* **1966**, *88,* 1113.

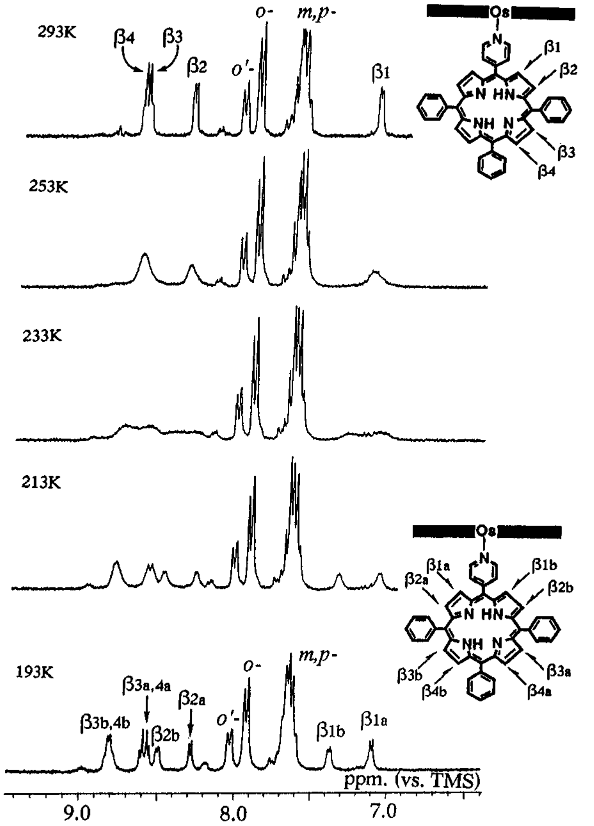

Figure 8. ^1H NMR spectra of pyrrole β-protons of Os(OEP)(CO)(H_2PyP_3P), **1**, at various temperatures.

interactions between the osmium ions in a molecule through the bridging ligand. Each osmium ion is oxidized or reduced independently.

With regard to tetraarylporphyrins (H_2PyP_3P, *cis*-$H_2Py_2P_2P$, *trans*-$H_2Py_2P_2P$, H_2Py_3PP, and H_2TPyP) of the oligomers, two reduction waves were observed at the potentials below *ca.* −1 V. The potentials and the peak separations were almost the same with those of free tetraarylporphyrin monomers,[59] which indicate the absence of interactions between the constituent porphyrin rings in each oligomer.

In comparing all the CV data more precisely, small but certain features were found on the reductions of tetraarylporphyrins. Two reduction steps for tetraarylporphyrins in this oligomer systems were observed at more positive potentials than the respective steps for the free monomer states. The largest positive potential shift was observed on **5**, which has four OEP rings in a molecule. The poor solubility of free tetraarylporphyrins in dichloromethane precluded from obtaining reliable comparative data in the same conditions. Data from the reference[60] were used for the comparisons of redox potentials. The data suggested that H_2TPyP was expected to have the first reduction potential at −0.96 V[61] which may be compared with the experimental value of H_2PyP_3P (−1.09 V).

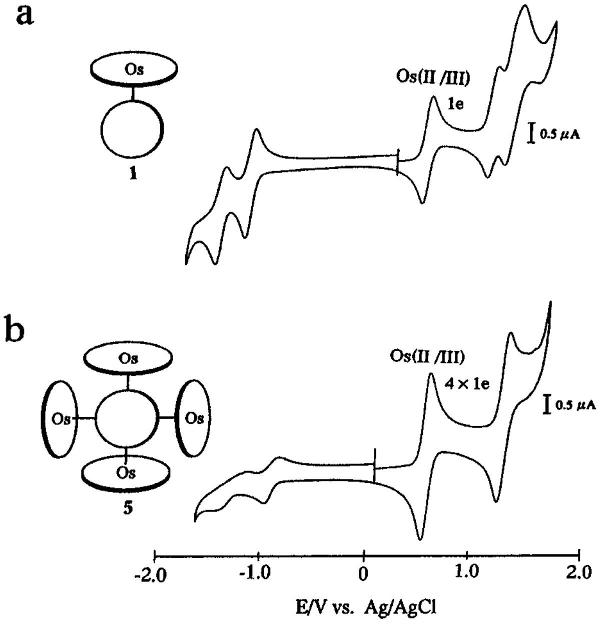

Figure 9. Cyclic voltammograms of the oligomers in dichloromethane containing 0.1 M $(TBA)PF_6$ (platinum electrode; scan rate 50 mV/s; vs Ag/AgCl): (a) Os(OEP)(CO)(H_2PyP_3P), **1**; (b) $[Os(OEP)(CO)]_4$(H_2TPyP), **5**.

In the oligomers, the first reduction occurs at −1.05 and −0.82 V for **1** and **5**, respectively. Thus we can estimate the positive shifts from free monomers {H_2PyP_3P or H_2TPyP} to be 0.04 {= −1.05 − (−1.09)} and 0.14 {= −0.82 − (−0.96)} V for **1** and **5**, respectively, or *ca.* 40 mV/(OEP ring). This trend {*ca.* 40 mV/(OEP ring)} fits well on the results of each oligomer (Table 3). The positive shift in redox potentials of the axial or bridging ligands are attributed to the electron-withdrawing ability of CO groups, which is at the *trans*-positions of the pyridyl groups. These results indicate that there are no electrochemical interactions between the component porphyrins.

Conclusion

A series of new osmium(II) porphyrin oligomers having a mixed 4-pyridyl- and phenyl-substituted porphyrin as an axial

---

(59) Williams, G. N.; Williams, R. F. X.; Lewis, A.; Hambright, P. *J. Inorg. Nucl. Chem.* **1979**, *41*, 41.

(60) The replacement of phenyl groups by pyridyl groups makes the free base porphyrin reduction process easier.[59] The first half-wave reduction potentials for H_2TPP and H_2TPyP were −1.56 and −1.38 V, respectively. Thus they differ by 180 mV, or 45 mV/(pyridyl group).

(61) $-1.09 \text{ V} + (0.045 \times 3) = -0.955 \text{ V} \approx -0.96 \text{ V}$.

or a bridging ligand were synthesized and characterized by UV−vis, IR, and ^1H NMR spectral methods and cyclic voltammetry. The UV−vis spectra and cyclic voltammograms showed little interaction between the constituting porphyrins visible spectrally and electrochemically. In ^1H NMR large high-field shifts were observed for some protons in axial or bridging porphyrins, which indicates their coordination to osmium with pyridyl groups. The ring current effect of OEP rings on ^1H NMR spectra enables to observe directly the tautomerization of internal N−H protons in the tetraarylporphyrin. The activation energy of N−H tautomerism, E_a, was evaluated to be 40.5 kJ mol^{-1} for Os(OEP)(CO)(H_2PyP_3P), **1**.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 08454206 and 06804034) from the Ministry of Education, Science, and Culture, Japan. A research grant from the 1994 Kawasaki Steel 21st Century Foundation is also gratefully acknowledged.

IC960878K