J. Am. Chem. Soc. 1994, 116, 11193−11194

Synthesis of "Wheel-and-Axle"-Type Porphyrin Arrays Composed of Phosphorus Porphyrins

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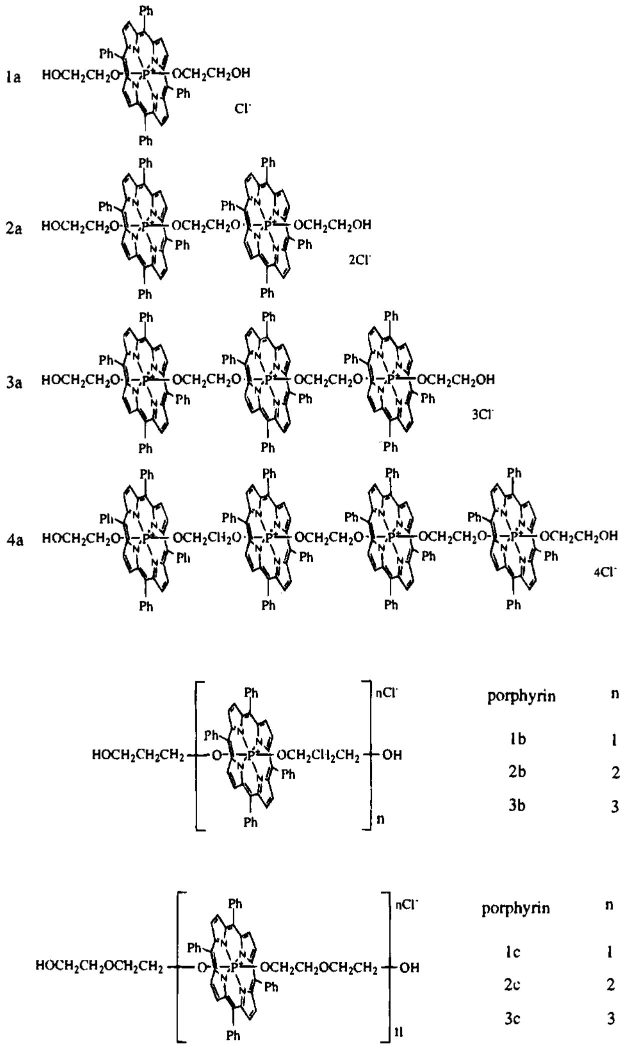
Received June 7, 1994

The synthesis and characterization of a series of large porphyrin oligomers are important not only for elucidation of the energy and/or the electron transfer functions of the photosynthetic reaction center[1,2] but also for application of the functions to molecular architecture.[2−4] In the construction of porphyrin oligomers, the distance and orientation between the porphyrin rings should be determined according to the functional requirements. For this reason, many porphyrin oligomers synthesized so far were fixed at their peripheral *meso* or *pyrrole-β* position by covalent bond(s),[2] although the systematic molecular architecture requires extensive synthetic efforts. To alleviate this, the utilization of the axial bond on the central atom of porphyrin could reduce the difficulty of the systematic construction of the porphyrin oligomers,[5,6] because the ligands with two coordination groups and the porphyrins with fifth and sixth coordination abilities can form the one-dimensional porphyrin array easily. However, many of the axial-bonding-type porphyrin oligomers obtained to date were solid-state polymers;[6] the ordered porphyrin oligomers were very difficult to synthesize and isolate because of unstable axial coordination and intractable properties. In the previous paper,[7] we reported the stable axial bond formation of non-metal phosphorus porphyrin. The axial bond is useful for fixing the porphyrin rings at various distances and orientations, and it could enable us to construct molecular architecture using porphyrins. In this paper, we report the systematic synthesis of novel "wheel-and-axle"-type phosphorus(V) porphyrin oligomers, whose porphyrin rings are separated by various lengths of stable axial bridges connected with the central phosphorus atoms.

Chart 1



The "wheel-and-axle"-type phosphorus porphyrin monomers (**1a−c**) and oligomers (**2a−c**, **3a−c**, and **4a**) (Chart 1) were synthesized *in one pot* by the condensation of the dichlorophosphorus(V) tetraphenylporphyrin[8] and the corresponding diol in refluxing butyronitrile for 3 days, where the elimination of hydrogen chloride afforded a mixture of the corresponding monomers and various lengths of oligomers. After the evaporation of the solvent, the reaction mixtures were purified and separated by column chromatography.[9] The yields of the monomers and oligomers were dependent on the initial concentrations of the dichlorophosphorus porphyrin and the corresponding diol. For the reaction of the dichlorophosphorus porphyrin in pure diol, only the monomer was obtained as reported previously.[7]

The obtained oligomers were characterized by ^{1}H-NMR and ^{31}P-NMR.[10] The proton signals located below 3 ppm were assigned to axial bridge protons, which were shifted to the upfield region by the large ring current of the porphyrin ring(s). Since the ring current shift appears to be an additive property from all porphyrin rings in the oligomer, the inner bridge protons were observed in the more upfield region. The phosphorus−proton couplings of the axial bridges imply that they are attached to the central phosphorus atom as expected. Peripheral proton signals of monomers (pyrrole-*β*, 8.94−9.01 ppm, d, 8H; phenyl, 7.2−8.1 ppm, m, 20H) were similar in

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[1] (a) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385. (b) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618. (c) Allen, J. P.; Feher, G.; Yeates, T. O.; Rees, D. C.; Deisenhofer, J.; Michel, H.; Huber, R. *Proc. Natl. Acad. Sci.* U.S.A. **1986**, *83*, 8589. (d) Krauss, N.; Hinrichs, W.; Witt, I.; Fromme, P.; Pritzkow, W; Dauter, Z.; Betzel, C.; Wilson, K. S.; Witt, H. T.; Saenger, W. *Nature* **1993**, *361*, 326.

[2] (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435 and references therein. For dimeric porphyrins formed by ligand-to-metal coordination, see: (b) Godziera, G. M.; Tilotta, D.; Goff, H. M. *Inorg. Chem.* **1986**, *25*, 2142. (c) Bied-Charreton, C.; Mérienne, C.; Gaudemer, A. *New J. Chem.* **1987**, *11*, 633. (d) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111. For large porphyrin oligomers, see: (e) Wennerstrom, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* **1989**, *30*, 1129. (f) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054. (g) Tran-Thi, T. H.; Lipskier, J. F.; Maillard, P.; Momenteau, M.; Lopez-Castillo, J.-M.; Jay-Gerin, J.-P. *J. Phys. Chem.* **1992**, *96*, 1073. (h) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618. (i) Prathapan, S.; Johnson, T. E.; Lindsey J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519.

[3] Hopfield, J. J.; Onuchic, J. N.; Beratan, D. N. *Science* **1988**, *241*, 817.

[4] For molecular architecture, see: (a) Chen, J.; Seeman, N. C. *Nature* **1991**, *350*, 631. (b) Mathias, J. P.; Stoddart, J. F. *Chem. Soc. Rev.* **1992**, 215. (c) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.

[5] For axial-bonding-type porphyrins, see: (a) Inoue, S.; Aida, T. *New Method for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum: New York, 1992, p 33. (b) Andersson, J. E.; Liu, Y. H.; Kadish, K. M. *Inorg. Chem.* **1987**, *26*, 4174.

[6] Hanack, M.; et al. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vol. I, p 133.

[7] Segawa, H.; Kunimoto, K.; Nakamoto, A.; Shimidzu, T. *J. Chem. Soc., Perkin Trans. 1* **1992**, 939.

[8] Marrese, C. A.; Carrano, C. J. *Inorg. Chem.* **1983**, *22*, 1858.

[9] The reaction mixtures were chromatographed on alumina with $CHCl_3$/CH_3OH (50:1−3:1, gradient) to remove some impurities. The main fractions containing the monomer and oligomers were further purified and separated by column chromatography using silica gel with $CHCl_3$/CH_3OH (10:1−3:1, gradient). The corresponding monomer, dimer, trimer, and tetramer were eluted in that order, and longer oligomers were eluted by CH_3OH.

0002-7863/94/1516-11193$04.50/0

Table 1. Absorption Maxima of Phosphorus Porphyrin Monomers and Oligomers in $CHCl_3$

	λ_{max}/nm		
porphyrin	Soret	Q(1,0)	Q(0,0)
1a	431	560	600
2a	425	561	604
3a	421	562	606
4a	420	562	607
1b	431	561	602
2b	425	562	604
3b	422	562	604
1c	432	561	603
2c	427	561	601
3c	425	561	602

terms of region and pattern to those of the reported phosphorus(V) tetraphenylporphyrin derivatives.[7] On the other hand, pyrrole-β proton signals of dimers (8.60–8.83 ppm, 16H) were shifted to the upfield region compared with those of the corresponding monomers, and pyrrole-β proton signals of trimers were also shifted upfield and split into signals for inner pyrrole-β protons (**3a**, 8.32 ppm; **3b**, 8.47 ppm; **3c**, 8.65 ppm; 8H) and outer pyrrole-β protons (**3a**, 8.50 ppm; **3b**, 8.79 ppm; **3c**, 8.80 ppm; 16H). The large upfield shifts depending on the bridge length suggest that the porphyrin rings are aligned and fixed in their axial position. From the integration intensities of the protons, the numbers of porphyrin rings in the oligomers can be confirmed. ^{31}P-NMR of oligomers around −180 ppm, which is in the typical range of hexacoordinated phosphorus compounds,[11] suggests that the two axial bridges are attached to each central phosphorus atom at the fifth and sixth coordination positions. Interestingly, phosphorus signals of trimer **3a** and tetramer **4a** were coupled via long-range interaction and split into triplet-doublet and multiplet-multiplet respectively. Consequently, it was confirmed that the obtained products were "wheel-and-axle"-type phosphorus(V) porphyrin oligomers, whose porphyrin rings were separated by various lengths of stable axial bridge(s) connected with the central phosphorus atoms.[12]

In $CHCl_3$ solution, all the derivatives show the normal porphyrin absorption spectra (supplementary material) and the Soret absorption maxima of the oligomers are blue-shifted compared with the corresponding monomers, depending on the number of porphyrin rings (Table 1).[13] The absorption properties of the porphyrin arrays are elucidated from the exciton coupling between the porphyrin rings, where the spectral shifts are described by Kasha's molecular exciton model.[14] Figure 1 shows the energy shift of the Soret absorption maxima of oligomers compared with that of the corresponding monomers. The energy shifts show a linear relationship with respect to the parameter of exciton coupling which is based on the numbers of porphyrin rings and assumes the parallel orientation of the porphyrin rings. The slopes are dependent on the bridge length of the oligomers, indicating that the one-dimensional array structures are realized in the "wheel-and-axle"-type phosphorus(V) porphyrin oligomers. This suggested that the axial bridge is capable of the keeping of the structure in $CHCl_3$ solution. It is noteworthy that the "wheel-and-axle"-type phosphorus(V) porphyrin oligomers show good solubility even in highly polar solvents such as H_2O/CH_3CN (95:5) because of the cationic charges on their central phosphorus atoms and the hydrophilicity of their terminal hydroxyl groups.[15] Interestingly, the lifetime of the singlet excited state of the "wheel-and-axle"-type phosphorus(V) porphyrin derivatives was obviously dependent on the numbers of porphyrin rings in the polar solvent (**1a**, 4.4 ns; **2a**, 4.2 ns; **3a**, 3.5 ns; in H_2O/CH_3CN (95:5)).[16] These results suggest that their excited-state properties are tunable systematically. The present method of synthesis is considered to be useful for the construction of molecular architecture using the porphyrin array.

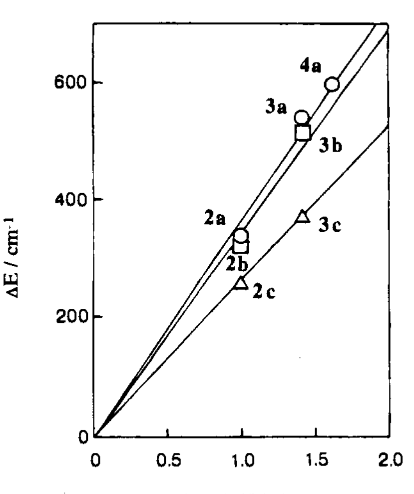

Figure 1. Plot of exciton shift energy ΔE versus $2\cos(\pi/(N+1))$.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Absorption spectra of **1a**, **2a**, **3a**, and **4a**, FAB mass spectra of **2a**, **2b**, and **2c**, and fluorescence decay of **1a**, **2a**, and **3a** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) ^{1}H- and ^{31}P-NMR data in $CDCl_3$ are relative to TMS and H_3PO_4, respectively. **1a**: ^{1}H δ −2.29 (dt, J_{P-H} = 10.8 Hz, 4H), 0.74 (m, 4H), 7.6–8.1 (m, 20H), 9.01 (d, J_{P-H} = 2.9 Hz, 8H); ^{31}P δ −180.9 (s). **1b**: ^{1}H δ −2.38 (dt, J_{P-H} = 11.9 Hz, 4H), −1.36 (m, 4H), 1.33 (t, 4H), 7.2–8.0 (m, 20H), 8.94 (d, J_{P-H} = 2.9 Hz, 8H); ^{31}P δ −179.9 (s). **1c**: ^{1}H δ −2.29 (dt, J_{P-H} = 11.4 Hz, 4H), 0.60 (m, 4H), 2.14 (t, 4H), 2.72 (t, 4H), 7.6–8.1 (m, 20H), 9.00 (d, J_{P-H} = 2.9 Hz, 8H); ^{31}P δ −181.3 (s). **2a**: ^{1}H δ −5.54 (m, 4H), −2.75 (dt, J_{P-H} = 13.2 Hz, 4H), 0.31 (m, 4H), 7.4–7.9 (m, 40H), 8.60 (br, 16H); ^{31}P δ −182.3 (s). **2b**: ^{1}H δ −4.43 (m, 6H), −2.26 (dt, J_{P-H} = 12.5 Hz, 4H), −1.57 (m, 4H), 1.32 (t, 4H), 7.6 (br, 40H), 8.68 (br, 16H); ^{31}P δ −180.9 (s). **2c**: ^{1}H δ −3.06 (m, 4H), −2.49 (dt, J_{P-H} = 11.4 Hz, 4H), −0.90 (m, 4H), 0.49 (m, 4H), 2.07 (t, 4H), 7.62 (br, 40H), 8.83 (d, J_{P-H} = 2.6 Hz, 16H); ^{31}P δ −181.6 (s). **3a**: ^{1}H δ −6.2 to −5.6 (m, 8H), −3.1 to −2.7 (m, 4H), 0.25 (br, 4H), 6.7–7.9 (m, 60H), 8.32 (br, 8H), 8.50 (br, 16H); ^{31}P δ −182.9 (d, J_{P-P} = 4.9 Hz), −185.4 (t). **3b**: ^{1}H δ −4.9 to −4.3 (m, 12H), −2.71 (dt, 4H), −1.8 to −1.4 (m, 4H), 1.16 (t, 4H), 6.9–8.0 (m, 60H), 8.47 (br, 8H), 8.79 (br, 16H); ^{31}P δ −181.1 (br), −182.7 (br). **3c**: ^{1}H δ −3.6 to −2.8 (m, 8H), −2.7 to −2.3 (m, 4H), −1.2 to −0.7 (m, 8H), 0.47 (br, 4H), 2.07 (t, 4H), 2.66 (t, 4H), 7.1–8.0 (m, 60H), 8.65 (br, 8H), 8.80 (br, 16H); ^{31}P δ −181.5 (br). **4a**: ^{1}H δ −6.8 to −5.7 (m, 12H), −3.2 to −2.7 (m, 4H), 0.31 (br, 4H), 6.4–7.9 (m, 80H), 8.0–8.8 (br, 32H); ^{31}P δ −182.8 (m), −185.9 (m).

(11) *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, **1987**; pp 369–402.

(12) The "wheel-and-axle"-type phosphorus(V) porphyrin derivatives were characterized by FAB mass spectra. The parent peak of each derivative coincided with the expected molecular weight in the absence of counterion. High-resolution mass spectral data for monomer **1a** is follows: FAB HRMS, *m/z* 765.2603 (M^+), calcd for $C_{48}H_{38}N_4O_4P$ 765.2629. The dimer structures were confirmed by FAB mass spectra (supplementary material). **2a**: FAB MS, *m/z* 1469 ($C_{94}H_{70}N_8O_6P_2$, $[M + 1]^+$). **2b**: FAB MS, *m/z* 1511 ($C_{97}H_{76}N_8O_6P_2$, $[M + 1]^+$). **2c**: FAB MS, *m/z* 1601 ($C_{100}H_{82}N_8O_9P_2$, $[M + 1]^+$). Since the number of carbon atoms in each dimer exceeds 90, the molecular ion peak shows the maximum at M + 1 by the contribution of a ^{13}C atom.

(13) The extinction coefficients of the Soret absorption for the oligomers (**2a**, 6.80×10^5; **3a**, 10.22×10^5) were slightly smaller than the corresponding multiple values for monomer (**1a**, 3.60×10^5).

(14) Kasha, M. *Radiat. Res.* **1963**, *20*, 55. For simplification, the ring orientation was assumed to be parallel.

(15) For each phosphorus(V) porphyrin oligomer solution of the polar solvent, an absorption shoulder was observed at the low-energy region of the Soret absorption, suggesting that undefined conformational change was induced in the polar solvent. Taking into account the relatively large shoulder of **2b** compared with those of **2a** and **2c**, the absorption shoulders are considered to be due to the porphyrin–porphyrin dihedral twist as a function of bridge conformation, where the oblique conformation is suitable for **2b** with an odd-numbered carbon bridge.

(16) Fluorescence lifetimes were measured on Horiba NAES-550 time-correlated single-photon counting equipment (supplementary material). The error values are less than 0.1 ns.