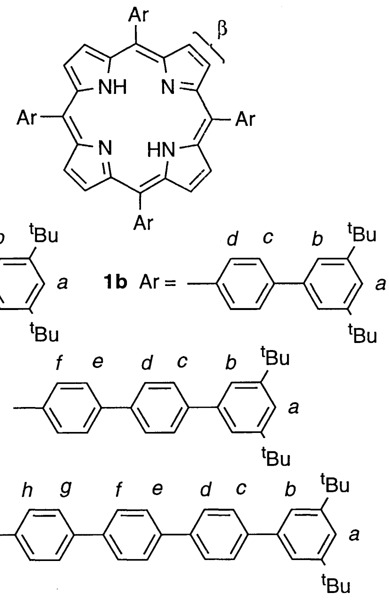
Synthsis and Properties of Oligo-*para*-phenylene Substituted Porphyrins

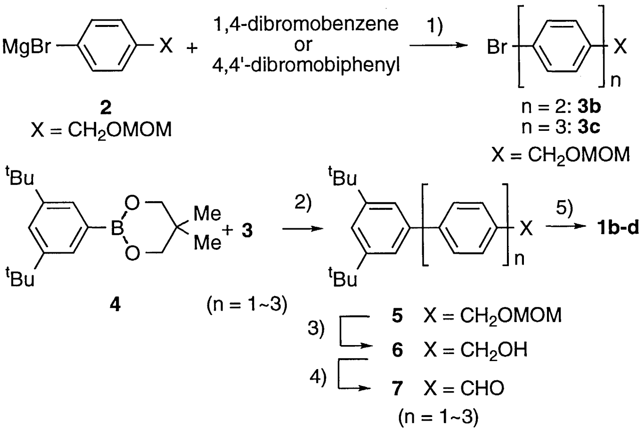
Shinji Mikami, Ken-ichi Sugiura, and Yoshiteru Sakata*
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567

(Received May 30, 1997; CL-970409)

A series of oligo-*para*-phenylene (OPP) substituted new porphyrins was prepared by the combinations of aryl coupling reactions and Lindsey's pyrrole condensation reactions. Low field shifts of OPP protons in ^{1}H-NMR spectra became larger when the protons locate closer to the center of the molecule.

Classical oligo- and poly-*para*-phenylene (OPP) chemistry is on stage as an important component molecule for photon-electron cooperative novel advanced materials.[1] To modify the electronic structure of OPP, phenylene unit is replaced by a wide variety of π-systems, *i.e.*, thiophene, carbazole, azulene, *etc.*[2] In this context, we designed OPP substituted new porphyrins **1**, which are large in size and rigid in structure based on molecular model considerations, and have narrow HOMO-LUMO gap.[3] Formally, cross shaped compound such as **1d** can be regarded as the extended OPP. In this communication, we wish to report the synthesis and some properties of a series of **1** and the corresponding metal complexes.[4] Since such molecules are expected to have low solubility toward usual organic solvents,[5] two *tert*-butyl (^{t}Bu) groups were introduced on each terminal phenyl ring of an OPP unit. These molecules are also expected to produce well-defined *nano-scale* materials because ^{t}Bu group is useful for the imaging of the molecules by a scanning tunneling microscope.[6,7]





1) 0.05eq. Pd(PPh$_3$)$_4$, THF.
2) 0.05eq. Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, PhMe-H$_2$O.
3) 0.1 eq. TsOH, MeOH-^{n}PrOH.
4) PCC, CH$_2$Cl$_2$.
5) (i) pyrrole, BF$_3$•OEt$_2$, CH$_2$Cl$_2$, (ii) DDQ.

Scheme 1.

The synthetic route of **1** except **1a**[8] is shown in Scheme 1. Important key intermediates **7** were prepared by using aryl cross coupling reactions. Thus, two OPP units **3b** and **3c** were obtained by treatment of Grignard reagent **2** with five equivalents of aryl dibromide in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ (51% yield for **3b**, 41% yield for **3c**). To introduce 3,5-di-*tert*-butylphenyl group into **3**, we employed improved Suzuki coupling reaction by boric acid ester **4** prepared from 3,5-di-*tert*-butylbromobenzene.[9,10] Deprotection of **5** was carried out with TsOH in methanol to give **6**. Subsequent oxidation reaction was applied to **6** to give the aldehydes **7** as air-sensitive solids. According to the standard Lindsey's method, the title porphyrins **1b-d** were prepared by Lewis acid (BF$_3$•OEt$_2$) catalyzed condensation reaction of **7** with pyrrole in dichloromethane, followed by oxidation reaction, in acceptable yields (43% for **1b**, 30% for **1c**, and 16% for **1d**).[11,12] All new porphyrins were characterized by spectroscopic methods[12] including laser desorption time of flights mass spectroscopy (M$^+$ = 1366 for **1b**, 1671 for **1c**, and 1975 for **1d**).

^{1}H-NMR spectra of **1** were shown in Figure 1. The chemical shifts of all the signals attributable to OPP units correlate with the distance between the proton and the porphyrin nucleus. Thus, the signals show lowfield shifts as the distance decreases. Apparently the strong diamagnetic ring current of the porphyrin nucleus is responsible for the lowfield shift. In the case of **1d**, the order of the shifts is given as follows; $h > g > f > e > d > c > b > a$. Comparing the series of **1**, the chemical shift of the terminal proton *a*, for example, changes from 7.44 (**1d**) to 7.78 ppm (**1a**). Interestingly, the chemical shifts of β-protons of porphyrin nucleus are gradually shifted to lower field, 8.95(**1d**) > 8.94 (**1c**) > 8.92(**1b**) > 8.80(**1a**), as the number of benzene rings of OPP increases.

The small electronic perturbation between porphyrin and OPP units is also supported by UV-vis. and electrochemical studies, as summarized in Table 1. The absorption of **1b-d** are superimposed of porphyrin and OPP chromophores. Only small differences in the intensities and the wavelengths of the

Table 1. UV-vis. and electrochemical data of **1**

	UV-vis.^{a} / nm in $CHCl_3$						Cyclic Voltammetry / V *vs.* Ag/AgCl in PhCN		
	OPP	Soret	Q-IV	Q-III	Q-II	Q-I	$[L^{-\bullet} Mn(III)] / [L^{2-} Mn(III)]$	$[L^{2-} Mn(III)] / [L^{2-} Mn(II)]$	$[L^{2-} Mn(II)] / [L^{3-\bullet} Mn(II)]$
1a		420.5	517.5	553.0	591.0	647.5	+1.45	-0.09	-1.36
		(5.72)	(4.26)	(4.01)	(3.68)	(3.81)			
1b	257.0	424.0	519.0	555.5	593.0	648.0	+1.51	-0.06	-1.31
	(4.82)	(5.74)	(4.29)	(4.13)	(3.79)	(3.78)			
1c	282.5	424.5	520.0	556.5	593.0	649.5	+1.54	-0.06	-1.33
	(4.98)	(5.72)	(4.27)	(4.14)	(3.76)	(3.77)			
1d	301.0	425.5	519.5	556.0	593.0	649.0	(*see text*)	-0.05	-1.29
	(5.18)	(5.74)	(4.30)	(4.17)	(3.79)	(3.79)			

^{a} Values in parentheses are log ε.

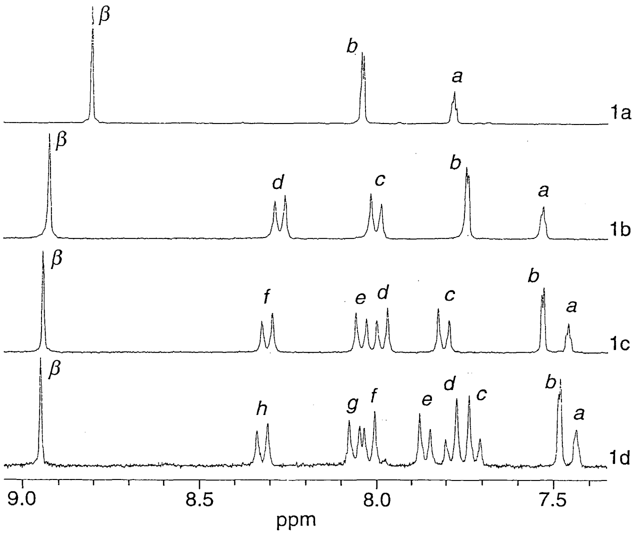


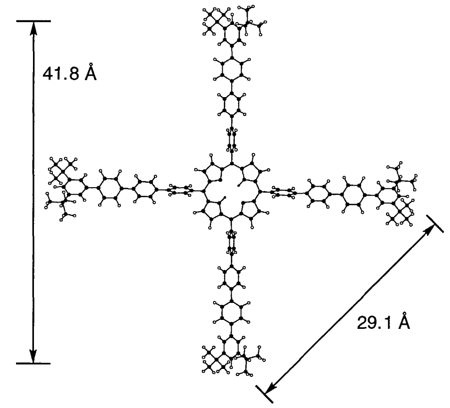
Figure 1. ^{1}H-NMR spectra of **1** in $(CDCl_2)_2$ at 127°C (270 MHz).

absorptions attributable to the porphyrin were observed. The intensities of the absorptions around 250~300 nm assigned to OPP units are nearly identical to the sum of the reported intensities for OPP.[13] Since low solubility of free base **1d** prevented the electrochemical studies, we performed cyclic voltammetry in benzonitrile for the corresponding manganese(II) complexes prepared by the reported method.[14] The reversible process at +1.45 V and the quasi-reversible one at -1.36 V are assigned as porphyrin π-centered redox for **1a**. Metal centered oxidation process was observed at -0.09 V as an inreversible process. For **1d**, unresolved broad oxidation wave was observed at around +1.4~1.7 V. We presume that this process contains five electron transfer reaction at four OPP units and one porphyrin π-system comparing with the reported values[15] and produces penta-cation radical.

We thank Dr. Tomohide Takami, Tohoku University, for several useful discussions. This work was supported in part by Ciba-Geigy Foundation (Japan) for the Promotion of Science and Grant-in-aide for Scientific Research from Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

1 J. Roncali, *Chem. Rev.*, **97**, 173 (1997).
2 P. Novák, K. Müller, K. S. V. Santhanam, and O. Haas, *Chem. Rev.*, **97**, 207 (1997).
3 CPK model considerations indicate that the sizes of **1d** are 41.8 Å in diagonal and 29.1 Å in side.



The size of other porphyrins are 33.1 X 23.7 Å for **1c**, 24.4 X17.4 Å for **1b**, and 15.6 X 11.2 Å for **1a**.
4 *meso*-Tetrakis(4-biphenylyl)porphyrin was reported in 1982; K. Yamashita, N. Kihara, H. Shimidzu, and H. Suzuki, *Photochem. Photobiol.*, **35**, 1 (1982).
5 I. A. Kathawalla, J. L. Anderson, and J. S. Lindsey, *Macromolecules*, **22**, 1215 (1989).
6 T. Takami, J. K. Gimzewski, R. R. Schlittler, T. Jung, Ch. Gerber, K. Sugiura, and Y. Sakata, *Abstracts of Papers, 50th National Meeting of the Japanese Physical Society*, Kanagawa; Japanese Physical Society: Tokyo, **1995**; Abstract 28p-PSB-29.
7 T. A. Jung, R. R. Schlittler, and J. K. Gimzewski, *Nature*, **386**, 696 (1997).
8 T. K. Miyamoto, N. Sugita, Y. Matsumoto, Y. Sasaki, and M. Konno, *Chem. Lett.*, **1983**, 1695.
9 P. Hodge, G. Power, and M. A. Rabjohns, *J. Chem. Soc., Chem. Commun.*, **1997**, 73.
10 S. Murphy, X. Yang, and G. B. Schuster, *J. Org. Chem.*, **60**, 2411 (1995).
11 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, and A. M. Marguerettaz, *J. Org. Chem.*, **52**, 827 (1987).
12 ^{1}H-NMR ($(CDCl_2)_2$, 270 MHz, 127±1 °C, δ); **1a**: 8.80 (s, 8H), 8.04 (d, 8H, J = 1.65 Hz), 7.78 (t, 4H, J = 1.65 Hz), 1.52 (s, 72H), and -2.50 (bs, 2H) ppm; **1b**: 8.92 (s, 8H), 8.27 (d, 8H, J = 8.24 Hz), 8.00 (d, 8H, J = 8.24 Hz), 7.74 (d, 8H, J = 1.65 Hz), 7.52 (t, 4H, J = 1.65 Hz), 1.49 (s, 72H), -2.47 (bs, 2H) ppm; **1c**: 8.94 (s, 8H), 8.31 (d, 8H, J = 8.24 Hz), 8.04 (d, 8H, J = 8.24 Hz), 7.98 (d, 8H, J = 8.24 Hz), 7.81 (d, 8H, J = 8.24 Hz), 7.53 (d, 8H, J = 1.65 Hz), 7.46 (t, 4H, J = 1.65 Hz), and 1.43 (s, 72H), and -2.46 (bs, 2H) ppm; **1d**: 8.95 (s, 8H), 8.32 (d, 8H, J = 8.24 Hz), 8.06 (d, 8H, J = 8.24 Hz), 8.02 (d, 8H, J = 8.24 Hz), 7.86 (d, 8H, J = 8.24 Hz), 7.79 (d, 8H, J = 8.24 Hz), 7.72 (d, 8H, J = 8.24 Hz), 7.48 (d, 8H, J = 1.65 Hz), 7.44 (t, 4H, J = 1.65 Hz), and 1.41 (s, 72H) ppm.
13 H. H. Jaffé and M. Orchin In "*Theory and Applications of Ultraviolet Spectroscopy*"; John Wiley & Sons, Inc. (1962); p 273. The band at 251.5 nm (log ε 4.26) is for biphenyl, 280 nm (log ε 4.40) is for terphenyl, and 300 nm (log ε 4.51) is for quaterphenyl.
14 R. D. Jones, D. A. Summerville, and F. Basolo, *J. Am. Chem. Soc.*, **100**, 4416 (1978).
15 A. Bohnen, W. Heitz, K. Müllen, H. J. Räder, and R. Schenk, *Makromol. Chem.*, **192**, 1679 (1991).