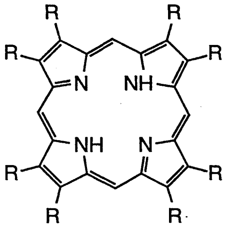
Synthesis and Properties of 2,3,7,8,12,13,17,18-Octakis(methylthio)porphyrin (OMTP)

Ken-ichi Sugiura, Murugaeson Ravi Kumar, Tavarekere K. Chandrashekar,[†] and Yoshiteru Sakata*
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567
[†]*Department of Chemistry, Indian Institute of Technology-Kanpur, Kampur 208-016, India*

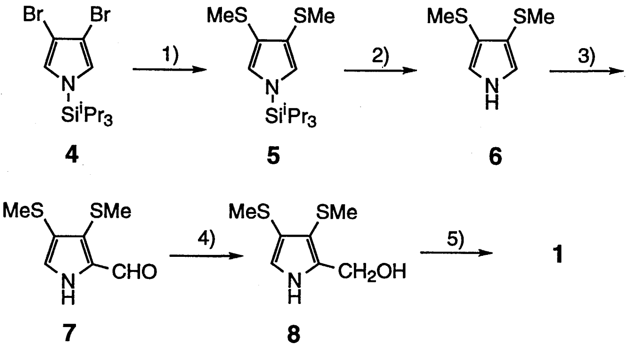
(Received December 9, 1996)

Porphyrins are important not only for biological pigments, but also for advanced materials.[1] In order to develop new functions or properties of porphyrins, the introduction of substituents at peripheral positions is required. Among various substituents, those with divalent chalcogen atoms are well known to constitute good π-electron systems such as tetrathiafulvalene derivatives. Furthermore, they produce chalcogen-chalcogen inter-atomic contacts which promote unique molecular alignments.[2] Although highly symmetric octamethoxyporphyrin (OMOP) **2** which has the same symmetry as that of octaethylporphyrin (OEP) **3** was reported,[3,4] the corresponding sulfur analog is not known. We designed and synthesized a new porphyrin, 2,3,7,8,11,12,17,18-octakis(methylthio)porphyrin (OMTP) **1**. This communication presents the synthesis and some properties of **1**.



1 R = SMe (OMTP)
2 R = OMe (OMOP)
3 R = Et (OEP)

The synthesis of OMTP is summarized in Scheme 1.[5] Pyrrole **5** was synthesized by treatment of **4**[6] with two equiv. of *n*-BuLi followed with dimethyl disulfide. Deprotection of **5** was carried out by treatment with *n*-Bu_4NF to give an important intermediate, 3,4-bis(methylthio)pyrrole (**6**). The pyrrole is unstable to air, but can be stored in dry box for several months. According to the standard reaction conditions for porphyrin synthesis, **6** was treated with formaldehyde in pyridine.[7] However, the desired OMTP was not obtained. Presumably, the weak electron withdrawing property of methylthio groups deactivates the reactivity of the pyrrole. We employed another tetramerization reaction reported by Ogoshi[8] and Ono[9] for the synthesis of porphyrins with electron withdrawing groups such as -C_nF_{2n+1}. Bis(methylthio)-pyrrole **8** was prepared by applying Vilsmeyer-Haack formylation reaction to **6** and subsequent reduction with $NaBH_4$. This pyrrole **8** was cyclized in the presence of dimethoxymethane with a catalytic amount of *p*-TsOH to give OMTP in acceptable yield. The corresponding nickel complex of **1** was obtained by the usual metal acetate method in quantitative yield.[10]



1) (i) 2eq. *n*-BuLi, THF, -78°, (ii) MeSSMe, 66% yield.
2) *n*-Bu_4NF, ether, quant. yield.
3) (i) DMF, $POCl_3$, CH_2ClCH_2Cl, (ii) AcONa aq., 85% yield.
4) $NaBH_4$, MeOH, ether, quant. yield
5) (i) $CH_2(OMe)_2$, *p*-TsOH, CH_2Cl_2, (ii) DDQ, 10% yield.

Scheme 1.

Selected spectroscopic data are summarized in Table 1. Due to large diatropicity of the porphyrin π-system, two characteristic singlets were observed in ^1H-NMR spectrum; one at high field assigned to the N-H protons, and the other at low field assigned to the *meso*-protons. The chemical shifts of the *meso*-protons of OMTP were shifted to downfield by 0.60 and 0.72 ppm

Table 1. ^1H-NMR and UV-vis data of OMTP and related compounds

	^1H-NMR / ppm in $CDCl_3$			UV-vis [a] / nm in toluene				
	meso	N-*H*	others	Soret	Q-IV	Q-III	Q-II	Q-I
OMTP	10.78	-3.16	3.13 (SC*H*$_3$)	433 (5.19)	531 (4.14)	570 (4.16)	599 (3.90)	659 (3.90)
OMOP [b]	10.06	-4.82	4.79 (OC*H*$_3$)	377 (5.19)	494 (3.98)	530 (4.09)	564 (3.76)	618 (3.78)
OEP [c]	10.18	-3.74	4.14 (-C*H*$_2$CH$_3$) 1.95 (-CH$_2$C*H*$_3$)	400 (5.20)	498 (4.15)	532 (4.03)	568 (3.83)	622 (3.76)

[a] Values in parentheses are logε. [b] from Ref. 4. [c] this work.

compared with the corresponding protons of OEP and OMOP, respectively. The inner N-H protons were also shifted to downfield by 0.58 and 1.25 ppm compared with the corresponding protons of OEP and OMOP, respectively. These results indicate the electron withdrawing nature of the introduced eight methylthio groups. On the other hand, upfield shift by 0.73 ppm was observed for SMe protons compared with thioanisole due to the large diamagnetic ring current of the porphyrin system.

The color of the crystals and a solution of OMTP is brown and is different from red-purple and blue color of OEP and OMOP, respectively. In the absorption spectra, Soret-band was observed at 433 nm in toluene. This value is shifted to longer wavelength by 33 nm and 56 nm as compared with OEP and OMOP, respectively. The bathochromic shift is due to the weak electron withdrawing character of methylthio groups as theoretically predicted[11] and as experimentally observed for fluorinated porphyrins.[12] All Q bands also showed bathochromic shifts. The relative intensity of the Q-bands (III>IV>II>I) is classified into Rhodo-type absorption. This phenomenon is also consistent with the nature of the introduced substituents. Fluorescence spectra in toluene showed their peaks at 663 and 773 nm with excitation at 433 nm.[13] However, the intensity was decreased to 37% compared with that of OEP by the introduction of eight divalent sulfur atoms.

This work was supported by Grant-in-Aide for Scientific Research on Priority Area (#253) "Novel Electronic States in Molecular Conductors" from Ministry of Education, Science, Sports, and Culture, Japan. MRK also appreciates the Association of International Education, Japan for the scholarship.

References and Notes

1 *Porphyrin and Metalloporphyrins*; 2 ed.; ed by K. M. Smith, Elsevier: Amsterdam (1975).

2 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geise, H. H. Wang, A. M. Kini, and M.-H. Whangbo, "*Organic Superconductor including Fullerenes*"; Prentice-Hall, Englewood Cliffs (1992), pp 210.

3 A. Merz, R. Schropp, and J. Lex, *Angew. Chem., Int. Ed. Engl.*, **32**, 291 (1993).

4 A. Merz, R. Schropp, and E. Dotterl, *Synthesis*, **1995**, 795.

5 All new compounds were characterized by ^{1}H and ^{13}C NMR, IR and mass spectra. ^{1}H-NMR (CDCl$_3$, 270 MHz, δ); **10**: 8.91 (bs, 1H), 6.75(d, J = 1.98Hz, 6H) and 2.30 (s, 6H) ppm; **11**: 9.84 (s, 1H), 9.33(s, 1H), 7.10 (d, J = 1.98 Hz, 1H), 2.47 (s, 3H) and 2.41 (s, 3H) ppm; **12**: 8.55 (bs, 1H), 6.80 (d, J = 2.97 Hz, 1H), 4.76 (s, 2H), 2.38 (s, 3H) and 2.29 (s, 3H) ppm; Nickel complex of **1**: 10.59 (s, 4H) and 3.02 (s, 24H) ppm.

6 B. L. Bray, P. H. Mathies, R. Naef, D. R. Solas, T. T. Tidwell, D. R. Artis, and J. M. Muchowski, *J. Org. Chem.*, **55**, 6317 (1990).

7 A. Treibs and N. Häberle, *Liebigs Ann. Chem.*, **718**, 183 (1968).

8 K. Aoyagi, H. Toi, Y. Aoyama, and H. Ogoshi, *Chem. Lett.*, **1988**, 1891.

9 N. Ono, H. Kawamura, M. Bougauchi, and K. Maruyama, *Tetrahedron*, **46**, 7483 (1990).

10 Ref. 1, pp798.

11 J. A. Shelnutt and V. Ortiz, *J. Phys. Chem.*, **89**, 4733 (1985).

12 M. Homma, K. Aoyagi, Y. Aoyama, and H. Ogoshi, *Tetrahedron Lett.*, **24**, 4343 (1983).

13 OEP showed fluorescence bands at 622 and 688 nm with excitation at 400 nm under the same conditions.