Porphyrin Architectures Constructed by CH···π Interactions: Synthesis and Crystal Structures of 5,10,15,20-Tetrakis(4-methylchalcogenophenyl)-21*H*,23*H*-porphyrins

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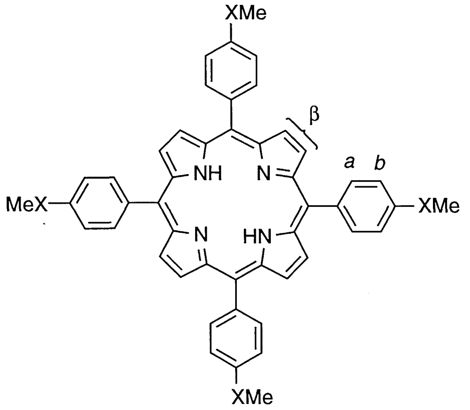
Tetraphenylporphyrins substituted with methylchalcogeno groups (XMe: X = Te, Se, S, and O) were prepared. Crystal structure analysis revealed that a novel type of molecular alignments was achieved by intermolecular CH···π interactions between XCH_3 and porphyrin π-systems.

In order to control molecular alignments of porphyrins, π-π[1,2] and hydrogen-bond[3] interactions as well as attractive forces between chalcogen atoms[4] have so far been employed. Here we report another example of attractive interactions usable to arrange porphyrins in crystals. Thus, we describe the synthesis and crystal structures of the tetraphenylporphyrins **1** substituted with methylchalcogeno groups, *i.e.*, XCH_3 (X = Te, Se, S, and O), in which the molecular alignments are controlled by CH···π interactions between XCH_3 and porphyrin π-systems.



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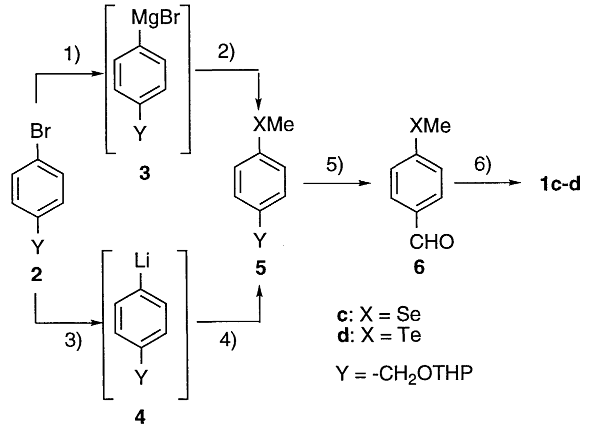
a: X = O **b**: X = S
c: X = Se **d**: X = Te

The preparation of **1a**[5] and **1b**[6] was carried out by the standard Adler-Longo reaction[7] with the corresponding commercially available benzaldehydes and pyrrole. The synthetic scheme of new porphyrins **1c** and **1d** is shown in Scheme 1. Introduction of chalcogen atoms was achieved by treatment of organometallic species with elemental chalcogen. Thus, the Grignard reagent **3** and lithium reagent **4** were treated with selenium and tellurium to give **5c** and **5d**, respectively. Subsequent deprotection and oxidation reactions were applied to **5** to give the important intermediates **6** which were characterized as 2,4-dinitrophenylhydrazone derivatives.[8] Although Linsey's porphyrin synthesis gave **1c** in more than 40% yield, low solubility of the product prevents the purification. Adler-Longo reaction was able to solve the problem, although the yield was low (18% yield). Trace amount of the tellurium analog **1d** was also obtained by the same method as quite unstable solid.



1) Mg, THF, 2) Se, THF, 3) ${}^tBuLi$, THF, 4) Te, THF
5) (i) 0.1 eq. PPTS, MeOH , (ii) $(CF_3CO)_2O$, DMSO, CH_2Cl_2
6) pyrrole, propionic acid

Scheme 1.

The results of ^1H-NMR and UV-vis. spectra are summarized in Table 1. In reflection with small differences in the chemical shifts of β-protons among **1**, small electronic perturbation of the substituents to the porphyrin π-systems through phenyl rings was observed in absorption spectra. However, all bands of **1** shifted to red compared with those of TPP. The intensities of Q-band for **1b-d** are Q-IV>Q-III>Q-I>Q-II and are similar to the reported values for **1a**.[9]

Table 1. ^1H-NMR and UV-vis. data of **1** and TPP

	^1H-NMR /ppm in $CDCl_3$					UV-vis.¶ / nm in chloroform				
	β	a§	b§	X-CH_3	N-*H*	Soret	Q-IV	Q-III	Q-II	Q-I
TPP	8.84	8.22	7.76		-2.78	417 (5.45)	516 (4.27)	550 (3.89)	591 (3.74)	648 (3.71)
1a	8.84	8.12	7.29	4.10	-2.75	423 (5.66)	520 (4.22)	557 (4.04)	594 (3.73)	651 (3.83)
1b	8.87	8.11	7.62	2.76	-2.79	425 (5.62)	520 (4.24)	557 (4.09)	593 (3.80)	651 (4.08)
1c	8.87	8.10	7.79	2.63	-2.80	425 (5.60)	519 (4.24)	556 (4.06)	593 (3.75)	650 (3.79)
1d†	8.87	8.04	7.99	2.48	-2.82	424	519	555	591	648

¶ Values in parentheses are log ε. § Multiplicities of the peaks for **1** are doublet, *J* = 8.5 Hz.
† Uv-vis. data are qualitative. Intensity of Q-band is Q-IV>Q-III>Q-I>Q-II.

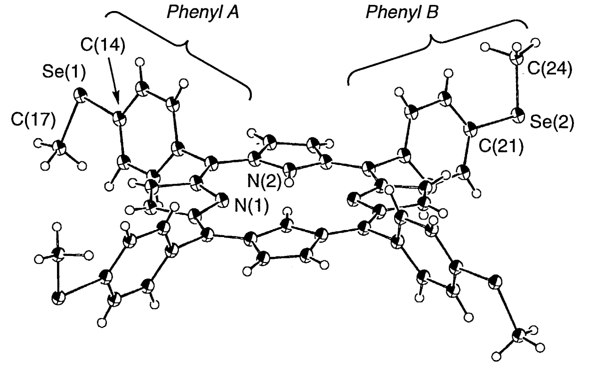


Figure 1. ORTEP drawing for **1c**. Thermal ellipsoids are at the 30% probability level. The crystallographically unique atoms are labeled. Selected bond distances (Å): Se(1)-C(14) 1.905(6), Se(1)-C(17) 1.91(1), Se(2)-C(21) 1.914(7), Se(2)-C(24) 1.78(2).

To obtain the structural details about the porphyrins, we performed the crystal structure analysis for **1b** and **1c**.[10] These molecules in crystal have *C2* axis perpendicular to the porphyrin nucleus. Least intermolecular chalcogen-chalcogen atomic distances were observed in [010] direction (4.172(3) Å for **1b** and 4.181(2) Å for **1c**). These values are longer than the sum of the van der Waals radius of the chalcogen atoms.[11] Therefore, there exist no special chalcogen-chalcogen atomic contacts as usually seen in TTF-based molecular conductors.

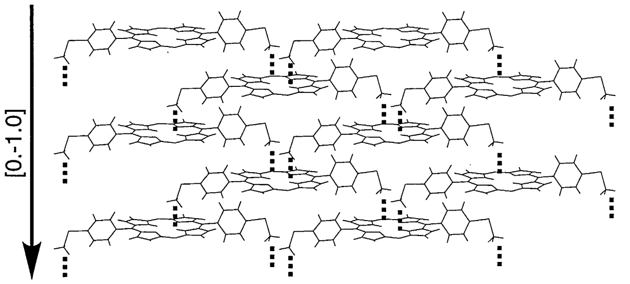


Figure 2. The packing of **1c**. The CH···π hydrogen bonds are indicated by the dotted lines. For clarity, solvent molecules and *phenyl A* of **1c** are omitted.

The crystals of **1b** and **1c** have novel and characteristic packing manners. Distances between C(24) and the least squares planes of the adjacent porphyrin ring formed by four nitrogen atoms are short (3.31 Å for **1b** and 3.33 Å for **1c**[12]) as compared with the value of van der Waals contact (3.5 Å: 1.7 Å for π-systems[1] and 1.8 Å for CH_3[13]). The results clearly show the existence of intermolecular CH···π interactions[14] in [0-10] direction between X-CH_3 and porphyrin π-systems (Figure 2). This is also supported by the following evidence. Thus, the intramolecular bond length of C(24)-Se(2) (1.78(2) Å) which is participating the CH···π interactions is significantly shorter than the C(17)-Se(1) bond length of **1c**, 1.91(1) Å, which is the typical for C(*sp3*)-Se bond.[15] For **1b**, the same tendency was observed (C(17)-S(1): 1.782(8) Å, C(24)-S(2): 1.739(9) Å). The above results can be explained by the *bond-length variation rule* proposed by Gutmann.[16] Thus, the hydrogen atoms activated by sulfur and selenium, *soft acid*, interact with the electron-rich porphyrin π-systems, *soft base*. The adjacent covalent bonds, C(24)-Se(2) and C(24)-S(2), become shorter. The packing pattern of **1c** is shown in Figure 2. One molecule interacts with two adjacent molecules and produces quasi two dimensional sheet structures. As far as our knowledge is concerned, these are the first example of CH···π interaction for porphyrin π-systems. Our findings will be applicable to the design of porphyrin based supermolecles.

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8 All new compounds were characterized by standard spectroscopic methods and the selected data are the followings. **6c**: ^{1}H-NMR ($CDCl_3$, 270 MHz): δ 9.81 (s, 1H), 7.61 (d, 2H, *J* = 8.2 Hz), 7.36 (d, 2H, *J* = 8.2 Hz), and 2.30 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 67.5 MHz): δ 191.0, 142.1, 133.5, 129.6, 128.4, and 6.3 ppm; IR (neat): 2828, 2737, 1697 cm^{-1}. Corresponding 2,4-dinitrophenylhydrazone: mp. 235-238 °C; ^{1}H-NMR: δ 11.32 (s, 1H), 9.15 (d, 1H, *J* = 2.4 Hz), 8.36 (dd, 1H, *J* = 2.4 and 9.6 Hz), 8.08 (d, 1H, 9.6 Hz), 8.08 (s, 1H), 7.65 (d, 2H, *J* = 8.2 Hz), 7.45 (d, 2H, *J* = 8.2 Hz), and 2.42 (s, 3H) ppm. **6d**: ^{1}H-NMR: δ 9.93 (s, 1H), 7.70 (d, 2H, *J* = 8.2 Hz), 7.65 (d, 2H, *J* = 8.2 Hz), and 2.28 (s, 3H) ppm; ^{13}C-NMR: δ 191.5, 135.0, 134.8, 129.6, 124.1, and -16.1 ppm; IR (NaCl): 2826, 2735, 1695 cm^{-1}. Corresponding 2,4-dinitrophenylhydrazone: dec. 210 °C; ^{1}H-NMR: δ 11.33 (s, 1H), 9.15 (d, 1H, *J* = 2.3 Hz), 8.36 (dd, 1H, J = 2.3 and 9.6 Hz), 8.08 (d, 1H, *J* = 9.6 Hz), 8.08 (s, 1H), 7.66 (d, 2H, *J* = 8.2 Hz), 7.57 (d, 2H, *J* = 8.2 Hz), and 2.27 (s, 3H) ppm.
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10 The highly unstable single crystals were mounted on a top of glass fiber and were placed quickly in the stream of cooled nitrogen. All measurements were made on a Rigaku AFC5R diffractomoter with a graphite monochromater equipped with a Rigaku low-temperature device. Selected crystal data are the followings. [**1b**][PhCl], $C_{54}H_{43}ClN_4S_4$, FW = 947.11, monoclinic, C2 (#5), MoKα, 0.25 X 0.25 X 0.25 mm^3, -80.0 ± 1.0 °C, a = 21.26(1), b = 9.46(1), c = 15.811(9) Å, β = 133.96(2)°, V = 2288(3) Å^3, Z = 2, R = 0.055 and Rw = 0.055 for 1749 independent reflections (I > 3.00σ(I)). [**1c**][PhCl], $C_{54}H_{43}ClN_4Se_4$, FW = 1099.25, monoclinic, C2 (#5), MoKα, 0.45 X 0.20 X 0.08 mm^3, -77.5 ± 1.0 °C, a = 21.476(7), b = 9.533(6), c = 15.542(6) Å, β = 132.60(2)° , V = 2342(1) Å^3, Z = 2, R = 0.051 and Rw = 0.052 for 1851 independent reflections (I > 3.00σ(I)).
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12 Intermolecular atomic distances between C(24) and N(1) were 3.599(10) Å for **1b** and 3.59 (1) Å for **1c**, respectively. These values are about 0.1 Å longer than the CH···N hydrogen bond criteria (3.50 Å); Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr., Sect B*, **40**, 159 (1984).
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