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Supporting Information

Porphyrins with a Carbosilane Dendrimer Periphery as Synthetic Components for Supramolecular Self-Assembly†

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X-ray crystal structure data

Fig. S1/S2 and Fig. S3 display the crystal structure of **3c** and **6a** with respect to the orientation of the unit cell.

Figs. S4 – S6 illustrate the distinctive T-shaped π - π interaction for the molecules **9bA** and **9bB**.

Table S1: Crystal and intensity collection data of **3b**·1/₄CH₂Cl₂, **3c**, **4a**, **6a**·2thf and **9b**·3.5EtOH

Table S2: Selected geometric features of intermolecular hydrogen bonds of 6a

Table S3: Structural parameters of the porphyrin cores of 3b, 3c, 4a, 6a and 9b

Fig. S7 shows a graphical illustration of a saddling distorted *para*-functionalized porphyrin.

NMR data

Fig. S8: Atom labelling for the NMR data.



Figure S1. Graphical representation of the orientation of the 2D layers formed by **3c**, view along the crystallographic *c* (above) and *b* axes (below), revealing that no π - π interactions are observed along the *c*-axes. Dotted lines indicate T-shaped π - π interactions as displayed in more detail in Figure 7 (manuscript). The terminal substituents at the Si atoms and all carbon-bonded hydrogen atoms are omitted for clarity. Labels *, ", ' and # refer to symmetry generated Si atoms of crystallographically independent molecules of the asymmetric unit of **3c**, label A to symmetry generated atoms of the asymmetric unit of **3c** and labels B–E to symmetry generated atoms.



Figure S2. Graphical representation of the orientation of the 2D layers formed by **3c**, view along the crystallographic *a* axes, revealing that no π - π interactions are observed along the *c*-axes. Dotted lines indicate T-shaped π - π interactions as displayed in more detail in Figure 7 (manuscript). The terminal substituents at the Si atoms and all carbon bonded hydrogen atoms are omitted for clarity. Labels *, ", ' and # refer to symmetry generated Si atoms of crystallographically independent molecules of the asymmetric unit of **3c**, label A to symmetry generated atoms of the asymmetric unit of **3c** and labels B–E to symmetry generated atoms of A labelled atoms.



Figure S3. Above: Graphical representation of a part of one 2D layer formed by **6a** in the solid state and its orientation with respect to the unit cell, illustrating the interaction of individual molecules of **6a** along approximately the crystallographic *b* axes due to intermolecular O-H-O hydrogen bonds and approximately along the crystallographic *a* axes by intermolecular O(H)–Zn coordinative bonds. Below: Graphical representation of parts of two adjacent 2D layers, illustrating the individual nature of the 2D layers. General remark: All carbon-bonded hydrogen atoms and packing solvent molecules are omitted for clarity. Of disordered atoms only one atomic position is displayed.

Figures S4 – S6, preliminary remark.

Below, three Figures are given which illustrates the distinctive T-shaped π - π interaction responsible for the interaction of molecules of **9bA** and **9bB** in the solid state structure of **9b** to form 2D layers as a part of the overall 3D network. Therefore, three molecules of **9bA** and two molecules of **9bB** are displayed in Figure S4 as a "cut-off" of the 2D layers. Thereby, two molecules of **9bA** approach one molecule of **9bB** in "up-and down" down fashion by T-shaped π - π interaction, indicated in yellow in Figure 4. This motif propagates further in linear elongation. Molecule **9bA** approaches **9bB** at a distance of ca. 16.1 Å, as determined by distance of geometrical centroids of the porphyrin cores. Additionally, Figure 4 displays indicated in pink the nearly analogous interaction of two molecules of **9bB** to one molecule of **9bA**. This motif propagates also further in linear elongation but nearly perpendicular to the one indicated in yellow, and consequently all interactions responsible for the formation of the 2D layers are displayed. Here, **9bB** approaches **9bA** at a distance of ca. 16.1 Å, as determined by distance of geometrical centroids of the porphyrin cores.

The individually displayed T-shaped π - π interactions in Figs. S5 and S6 must be questioned. Certainly, the approach of one phenyl ring of one molecule to the porphyrin core of a second molecule represents clearly T-shaped π - π interactions, as centroids-to-centroid distances and interplanar angles of interaction groups match requirements well. In case of the other displayed π - π interactions this situation is different, as especially the interplanar angles deviate severly from 90°. However, these interactions are indicated as well. Finally it needs to emphasized that in both Figure S5 and S6 one type of T-shaped π - π interactions, as displayed in Figure 14 in the manuscript, is not illustrated due to clarity.

The labelling code used in Figs. S4-S6 corresponds to those indicated in the manuscript. The third individual molecule of 9bA is labelled as follows:

1st half: N1, N2, Si1-Si8, C1-C83 labelled with suffix "C"

2nd half:N1A, N2A as N1AC, N2AC

Si1A-Si8A and C10A-C83A as Si1%-Si8% and C10%-C83%.



Figure S4. Graphical representation of a part of one 2D layer as a part of the 3D network formed by **9b** in the solid state. Illustrated is the interaction of two molecules of **9bA** (involving the atoms N1 and N2 and symmetry generated ones) to **9bB** (involving the atoms N3 and N4 and symmetry generated ones) indicated in yellow colour, and of two molecules of **9bB** to **9bA** indicated in pink colour, respectively, by T-shaped π - π interaction of phenyl groups to the porphyrin cores as well as between phenyl groups. General remark: All hydrogen atoms, packing solvents and terminal Si-functionalities are omitted for clarity.



Figure S5. Graphical illustration of the T-shaped π - π -interaction of two molecules of **9bA** with one molecule of **9bB** as a cut-off of the 2D motif. The sign < refers to the calculated interplanar angles between set of atoms adjoining differently coloured areas and the value D gives the calculated distances of corresponding geometrical centroids. All hydrogen atoms and the terminal Si-functionalities are omitted for clarity. The atomic labelling of the carbon atoms refers to the code of crystallographically independent **9bA** and **9bB** and includes symmetry generated equivalents as outlined in the preliminary remark.



Figure S6. Graphical illustration of the T-shaped π - π interaction of two molecules of **9bB** with one molecule of **9bA** as a cut-off of the 2D motif. The sign < refers to the calculated interplanar angles between set of atoms adjoining differently coloured areas and the value D gives the calculated distances of corresponding geometrical centroids. All hydrogen atoms and the terminal Si-functionalities are omitted for clarity. The atomic labelling of the carbon atoms refers to the code of crystallographically independent **9bA** and **9bB** and includes symmetry generated equivalents as outlined in the preliminary remark.

	3b·1/4CH2CI2	3c	4a	9b·3.5EtOH	6a∙2thf		
Empirical formula	C257H282Cl2N16Si16	$C_{72}H_{78}N_4Si_4$	$C_{64}H_{68}N_4Si_4Zn$	$C_{366}H_{454}N_8O_7Si_{32}$	$C_{72}H_{92}N_4O_6Si_4Zn$		
Formula weight	4115.33	1111.74	1070.95	5976.28	1287.23		
Crystal size (mm ³)	$0.4 \times 0.3 \times 0.3$	$0.2 \times 0.2 \times 0.1$	$0.4 \times 0.3 \times 0.04$	$0.2 \times 0.04 \times 0.04$	$0.25 \times 0.20 \times 0.18$		
Radiation/wavelenght (A)	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073	Μο Κα, 0.71073	Cu Kα, 1.54184		
Crystal system	tetragonal	triclinic	tetragonal	triclinic	triclinic P ¹		
Space group	<i>P4</i> ₃	P^{1}	P 4 ₃	P^{1}			
a (Å)	17.654(8)	10.524(7)	17.6235(7) 15.0021(10)		13.168(2)		
$b(\mathbf{A})$	17.654(8)	10.624(5)	17.6235(7)	25.1408(1)	13.595(2)		
<i>c</i> (Å)	19.697(13)	18.868(9)	19.6718(15)	28.4875(11)	20.215(4)		
α (°)	90	78.442(13)	90	111.449(8)	75.817(15)		
β (°)	90	87.750(12)	90	90.029(4)	76.980(16)		
γ (°)	90	65.942(10)	90	107.324(4)	80.566(14)		
Volume (Å ³)	6139(6)	1885.1(17)	6109.8(6)	9474.1(7)	3395.5(11)		
Ζ	1	1	4	1	2		
d_{calc} (g/cm ³)	1.093	0.979	1.164	1.047	1.259		
Temperature (K)	183(2)	298(2)	298(2)	205	100		
μ , mm ⁻¹	0.159	0.116	0.521	0.156	1.603		
F(000)	2194	594	2264	3210	1372		
θ (min/max) (°)	1.55/25.00	2.12/24.99	1.55/25.00	2.84/25.00	3.38/60.47		
Index range	$-14 \le h \le 14, \ 0 \le k \le 20,$	$-12 \le h \le 12, -12 \le k \le 12,$	$-14 \le h \le 15, 0 \le k \le 20,$	$-17 \le h \le 17, -29 \le k \le 29,$	$-14 \le h \le 14, -14 \le k \le 15,$		
Index Tange	$-23 \le l \le 23$	$0 \le l \le 21$	$-23 \le l \le 23$	$-33 \le l \le 33$	$-22 \le l \le 22$		
Reflection collected, unique	25129/10766	17013/6430	46414/10659	71422/30684	25781/9976		
$R_{\rm int}$	0.0814	0.0301	0.0702	0.0453	0.0177		
Data/restraints/parameters	10766/179/745	6430/324/497	10659/214/763	30684/384/1973	9976/98/837		
$R_1, wR_2 (I > 2\sigma(I))$	0.0557, 0.1231	0.0721, 0.2033	0.0536, 0.1278	0.0857, 0.2552	0.0661, 0.1871		
R_1 , wR_2 (all data)	0.1334, 0.1434	0.0888, 0.2209	0.1069, 0.1441	0.1406, 0.2776	0.0795, 0.2008		
GOF	0.911	1.092	0.967	1.067	1.104		
^{a)} R1 = $\frac{\sum \ F_o\ - \ F_c\ }{\sum F_o }$. ^{b)} wR2 = $\sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$ with $w = \frac{1}{\sigma^2(F_o^2) + (g_1P)^2 + g_2P}$; $P = \frac{(max(F_o^2, 0) + 2F_c^2)}{3}$							

Table S1. Crystal and Intensity Collection Data of 3b·¼CH₂Cl₂, 3c, 4a, 6a·2thf and 9b·3.5EtOH.

D–H […] A	D A	D–H […] A
02–H2 O3 ⁱ	2.509	152.9
02–H2 O3 ⁱⁱ	2.795	133.7
03–H3 O3 ⁱ	2.297	98.7
01–H1 O3 ⁱⁱⁱ	3.025	127.3

Table S2. Selected bond lengths (Å) and angles (°) of intermolecular hydrogen bonds of **6a**.^{a)}

Symmetry codes: i = 2 - x, -y -1, -z. ii = 4 - x, -y -1, -z. iii = 2 - x, -y, -z.

a) A comment is required as selected geometrical values of intermolecular hydrogen appear unusual. For example, the $O3-O3^i$ distance is with 2.297 Å to short for such a kind of hydrogen bonds and, furthermore, for example, the angle $O3-H3-O3^i$ is with 98.7 ° far away from the ideal value of 180 °. These strong deviations from reasonable values are caused by the, at least partially refineable, disorder of terminal OH functionalities and additionally by the fact that all oxygen bonded hydrogen atoms could not be located in difference Fourier maps but were inserted on idealized positions only. Furthermore, values given in this Table do not acknowledge hydrogen bonds of or to respective disordered atoms of O1 to O3, as even these data appear as very unusual. However, the data given here should verify indeed that between terminal Si-(CH₂)₃-OH groups of **6a** the formation of intermolecular hydrogen bonds is observed.

Figure S7, preliminary remark

A specific feature of (metallo) *meso*-tetraphenylporphyrins is, among other distortions, the so called saddling distortion, as ongoing studies did reveal that originally planar meso-tetraphenylporphyrins became significantly distorted, when deposited by vacuum techniques on appropriate wafers.^[ia] The different types of possible distortions are already explicitly described and illustrated by a report of Jentzen et al. along a series of nickel(II) meso-tetrasubstituted porphyrins^[ii]. Thus, the aim of the discussion added below is not to introduce another procedure to describe distortions of porphyrins but to give geometrical data of the here described porphyrins in a way that they become comparable with data delivered by scanning tunneling microscopy studies.

In order to illustrate a saddling distorted *meso*-tetraphenylporphyrin, Figure 15 displays such a porphyrin in two different views, defining thereby the angles α and β graphically. It is thereby assumed that the carbon atoms at the positions 5, 10, 15 and 20 of the C₂₀N₄ porphyrin core remain nearly non-involved by the saddling distortion and can be thus used to define a mean plane (plane I). The interplanar angles between individual pyrrole rings and plane I are then assigned as the angles β . Furthermore, the interplanar angles between the four annellated C₆H₄ aromatic rings and plane I are assigned as the angles α .

The molecular structures of the here discussed (metallo) *meso*-tetraphenylporphyrins **3b,c**, **4a**, **6a** and **9b** clearly indicate the here structurally described porphyrins to be not affected by any type of distortions. This becomes obvious when inspecting the bond angles of, for example, the atoms around the positions 5, 10, 15 and 20 of the $C_{20}N_4$ porphyrin cores (Table 3). Table 3 includes furthermore the sum of bond angles around the discussed carbon atoms expressed by the symbol Σ . As all values of *S* are 360.0°, at least within standard deviation, it can be concluded that all porphyrins

described within this study are planar. Furthermore, Table S3⁺ contains calculated mean planes of the C₂₀N₄ core atoms of **3b**, **c**, **4a**, **6a** and **9b** the root-mean-square deviation from planarity, the highest deviation from planarity observed for the specified atoms and calculated angles β according to Figure 15. All of these data illustrate in addition the pronounced planarity of the central $C_{20}N_4$ cores of **3b,c**, **4a**, **6a** and **9b**. This observation confirms related findings made for, *e.q.*, 5,10,15,20tetrakis-(phenyl)porphyrin (H₂TPP),^[iii] 5,10,15,20-tetrakis(4-methylphenyl)porphyrin,^[iv] 5,10,15,20tetrakis(4-methoxyphenyl)porphyrin^[v] on one hand and Zn(II)-TPP^[vi] on the other hand, which do all possess planar C₂₀N₄ cores in the solid state. Moreover, tetraarylporphyrins are often observed to be planar, even in the case that they are co-crystallized with different guest molecules as reviewed for over 200 different cases by Byrn et al.[vi] Despite this, it needs to be emphasized that saddling distorted (metallo) meso-tetraphenylporphyrins have been frequently described as, e.g., H₂TPP^[vii], tetrahydroxyphenyl-porphyrin^[viii] and Zn(II)-TBrPP (TBrPP = tetrakis(4-bromophenyl)porphyrin)^[ix]. The observation that H₂TPP can exhibit in the solid state either a planar or saddling conformer should underline the importance of the crystallographic characterization of respective (metallo) mesotetraphenylporphyrins in order to compare their structures in the solid state with those obtained after sublimation on wafers. Such a work is currently undergoing in our laboratories by making use of the here described porphyrins and related species.^[ia]



Figure S7. Graphical illustration of a saddling distorted *para*-functionalized 5,10,15,20-tetraaryl-substituted porphyrin together with the definition of the angles α and β .^[ib]

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a) L. Smykalla, P. Shukrynau, M. Hietschold, C. Mende, T. Rüffer, H. Lang "Manipulation of the electronic structure by reversible dehydrogenation of tetra(p-hydroxyphenyl) porphyrin molecules", to be submitted; b) This Figure displays a DFT calculated "saddle-shaped" deformed molecule of tetra(p-hydroxy-phenyl) porphyrin, of which all hydrogen atoms are omitted for clarity.

Table S3. Selected structural parameters of 3b,c, 4a, 6a and 9b.

planarity of the C ₂₀ N ₄ porphyrin cores				dimensions of the saddle-shape deformation of the $C_{20}N_4$ porphyrin cores							
	3b	3c	4a	6a	9b		3b ⁴	3c ⁵	4a ⁶	6a ⁷	9b ⁸
rmsd/	0.040 Å/	0.042 Å/	0.030 Å/	0.070 Å/	0.058 Å/	rmsd/	0.000 Å/	0.029 Å	0.025 Å/	0.006 Å/	0.000 Å/
hdp1	0.090(4) Å	0.076(2) Å	0.054(6) Å	0.148(3) Å	0.084(4) Å	hdp ²	0.000 Å	0.029(2) Å for C6	0.025(2) Å	0.007(2) Å	0.000 Å.
	for C3	for C8	for C7	for C5	for C4.				for C10	for C2	0.000 Å/
					0.056 Å/						0.000Å
					0.084(4)Å						
					for C104						
						β^3	1: 4.40(5)°	1: 1.6(1)°	1: 1.19(2)°	1: 3.4(3)°	1:2.3(3)°
							2: 2.34(5)°	2: 3.6(1)°	2: 3.13(4)°	2: 6.6(2)°	2: 3.0(3)°.
							3: 0.55(4)°		3: 2.28(4)°	3: 0.8(2)°	3: 1.9(4)°
							4: 2.27(4)°		4: 0.81(2)°	4: 3.2(3)°	4: 3.1(3)°

1) rmsd = \underline{root} -mean- \underline{s} quare \underline{d} eviation from planarity of calculated mean planes of atoms adjoining the porphyrin core. hdp = \underline{h} ighest \underline{d} eviation from planarity observed for specified atoms given in Å. 2) A mean plane of the four carbon atoms of the C₂₀N₄ porphyrin cores at the 5,10,15,20-annellated positions has been calculated (plane I). 3) Angle \mathbb{P} defines interplanar angles between plane I and calculated mean planes of respective pyrol rings. 4) Atoms adjoining plane I: C5, C10, C5A, C10A. Atoms adjoining pyrrole rings = 1: N1, C2-C5. 2: N2, C7-C10. 3: N3, C12-C15. 4: N4, C17-C20. 5) Atoms adjoining plane I: C1, C6, C11, C16. Atoms adjoining pyrrole rings = 1: N1, C1-C4. 2: N2, C6-C9. 6) Atoms adjoining plane I: C5, C10, C15, C20. Atoms adjoining pyrrole rings = 1: N1, C1-C4. 2: N2, C6-C9. 3: N3, C11-C14. 4: N4, C16-C19. 7) Atoms adjoining plane I: C2, C7, C12, C17. Atoms adjoining pyrrole rings = 1: N1, C1, C18-C20. 2: N2, C3-C6. 3: N3, C8-C11. 4: N4, C13-C16. 8) Atoms adjoining plane I: C5, C49, C5A, C49A.C105, C149, C5#, C49#. Atoms adjoining pyrrole rings = 1: N1, C1-C4. 2: N2, C6-C9. 3: N3, C101-C104. 4: N4, C106-C109.







2b,c

3b,c 4a,b





Figure S8. Atom numbering scheme of synthesized compounds (NMR data).