Porphyrians with a carbosilane dendrimer periphery as synthetic components for supramolecular self-assembly†

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The preparation of the shape-persistent carbosilane-functionalized porphyrins H2TPP(4-SiR’Me)4, Zn(II)-TPP(4-SiR’Me)4 (R = R’ = Me, CH2CH2=CH2, CH2=CHCH2OH; R = Me, R’ = CH2CH=CH2, CH2=CHCH2OH; TPP = tetraphenyl porphin), H2TPP(4-Si(C6H4-1,4-SiR’Me)3)4 and Zn(II)-TPP(4-Si-(C6H4-1,4-SiR’Me)3)4 (R = R’ = Me, CH2CH=CH2; R = Me, R’ = CH2CH=CH2) using the Lindsey condensation methodology is described. For a series of five samples their structures in the solid state were determined by single crystal X-ray structure analysis. The appropriate 0th and 1st generation porphyrin-based 1,4-phenylene carbosilanes form 2D and 3D supramolecular network structures, primarily controlled by either π-π interactions (between pyrrole units and neighboring phenylene rings) or directional molecular hydrogen recognition and zinc-oxygen bond formation in the appropriate hydroxyl-functionalized molecules. UV-Vis spectroscopic studies were carried out in order to analyze the effect of the dendritic branches on the optical properties of the porphyrin ring.

Introduction

Highly branched macromolecular architectures as well as self-assembly processes have become very popular and represent fascinating research areas both in natural sciences and engineering.1 In this respect, dendrimers and metallo-dendrimers, repetitive branched molecules of structural perfection, have attracted considerable attention as nanoscale molecular materials due to their novel properties.2 Dendrimers possess a three-dimensional and well-designed highly symmetric spherically arranged flexible structures employing isotropic assembling processes.3 In the past, also snowflake-shaped dendrimers containing rigid backbones within the dendrimer side chains were prepared.4 Such systems were used, for example, as mediators in electron-transfer and energy-transfer processes,5 as dendritic boxes6 or as drug carrier systems.7 Porphyrins can successfully be used as core molecules, as branching units, or, for example, in the stepwise synthesis of cross-shaped covalent assemblies.8 The micro-environments set-up by such molecules can be used among others to tune and control both optical and electrochemical properties of the appropriate porphyrin building block.8,9 Out of this, porphyrins are very useful molecules to probe and hence to characterize dendritic local environments. Recently, metallo-porphyrins tailored at a dendrimer core have been developed as synthetic models to mimic naturally occurring systems including light-harvesting and electron transfer processes (I.e., chlorophyll),10 molecular oxygen storage and transport phenomena (I.e., hemoglobin) as well as oxidation enzymes (I.e., cytochrome c).11,12 In such systems, the porphyrin building blocks have site isolation effects imposed by the dendritic shell. This makes it possible to utilize such species in diverse applications including homogeneous catalysis,13 drug delivery14 and singlet oxygen generation.14 In addition, these compounds can be applied as non-linear optical,16 and light-emitting17 materials, as molecular sensors18 or photo-active systems which can be considered as artificial antennae devoted to solar energy conversion.19
Recently, we got interested in the synthesis of SiCH₂CH₃ and Si(CH₂)₃OH-functionalized tetraphenyl porphyrins and to use them as supramolecular tectons in the formation of ordered network arrays, since this family of compounds provides a relatively unexplored class of molecules due to their large size, ease of preparation and, for example, excellent coordination ability. Out of these reasons, we here report the Lindsey condensation methodology for the preparation of novel 0th and 1st generation 1,4-phenylene-based carbosilane dendrimer-functionalized porphyrins and zinc(II)-porphyrins. The single-crystal X-ray structure determination of five samples is reported as well showing different interporphyrin interactions.

**Results and discussion**

**Synthesis**

For the preparation of the carbosilane dendrimer-based porphyrins 3a-c (Scheme 1) the synthetic methodology developed by Lindsey was used. In this respect, the carbosilane aldehydes H(O)C-1-C₆H₄-4-SiRR′Me (2a, R = R′ = Me; 2b, R = Me, R′ = CH₂CH=CH₂; 2c, R = R′ = CH₂CH=CH₂), accessible by the consecutive treatment of 1-Br-C₆H₄-4-SiRR′Me (1a, R = R′ = Me; 1b, R = Me, R′ = CH₂CH=CH₂; 1c, R = R′ = CH₂CH=CH₂) with tBuLi and dimethylformamide, were reacted with pyrrole in the presence of catalytic amounts of [BF₃·OEt₂] followed by addition of 2,3-dichloro-5,6-dicyanobenzoquinone (= DDQ) in CH₂Cl₂ solutions at ambient temperature (Scheme 1, Experimental section). The appropriate porphyrins H₂TPP(4-SiRR′-Me)₄ (3a, R = R′ = Me; 3b, R = Me, R′ = CH₂CH=CH₂; 3c, R = R′ = CH₂CH=CH₂; TPP = tetraphenyl porphyrin) were isolated as dark red solids with yields of between 25 and 30% (see the Experimental section). The corresponding zinc(II)-porphyrins Zn-TPP(4-SiRR′Me)₄ (4a, R = Me, R′ = CH₂CH=CH₂; 4b, R = R′ = CH₂CH=CH₂) were obtained in virtually quantitative yields upon treatment of 3b or 3c with zinc(II) acetate in a mixture of CHCl₃-MeOH (ratio 5:1, v/v) (Scheme 1, see the Experimental section).

Scheme 1 Synthesis of 2–6.21–24
Porphyrsins 3b and 3c, respectively, with their terminal SiCH₃CH=CH₂ units could successfully be converted to the corresponding Si-propanolic-functionalized porphyrins 5a and 5b by a consecutive hydroboration–oxidation procedure (Scheme 1, see the Experimental section). Hydroboration of the appropriate end-grafted allyl groups with [BH₃·dms] (dms = dimethyl sulfoxide) in thf gave the corresponding BH₂-functionalized systems, which on addition of hydrogen peroxide were oxidized to the respective alcohols H₂TPP(4-SiRR″Me)₄ (Scheme 1). These porphyrsins produce, when reacted with the transition metal salt [Zn(OAc)₂·2H₂O], the expected zinc(ii) species Zn(II)-TPP(4-SiRR″Me)₄ (6a, R = Me, R″ = CH₂CH₂CH₂OH; 6b, R = R″ = CH₂CH₂CH₂OH) (Scheme 1). After appropriate work-up, aldehydes 8a–c were obtained in excellent yield, and porphyrins 3, 5 and 9 in yields between 25 and 40%, while the formation of the respective zinc(ii)-porphyrsins 4, 6 and 10 was quantitative (see the Experimental section). All carbosilane-functionalized (metal)porphyrsins are, as the aldehyde starting materials, dark red colored solids soluble in most common polar organic solvents. They are air- and moisture-stable with decomposition or melting points between 200 and 350 °C (see the Experimental section). Aldehydes 8 and porphyrsins 3–6 and 9–10 were characterized by elemental analysis, IR, UV-Vis and NMR spectroscopy (¹H, ¹³C{¹H}, ²⁹Si{¹H}) (see the Experimental section). ESI-TOF mass spectrometric measurements were additionally carried out with selected metal-free and zinc(ii) metallated samples.
The IR spectra of the newly synthesized allyl carbosilane-based porphyrins (Schemes 1 and 2) show a characteristic νC–C vibration at ca. 1630 cm⁻¹ together with one or two typical absorptions in the range of 800–840 cm⁻¹ for the Si–C stretching vibrations (see the Experimental section). The CH₃ bending vibration of the SiMe₃ entities (n = 1, 2, 3) is observed at ca. 1250 cm⁻¹. These findings are in agreement with allyl-functionalized carbosilanes, i.e. Si(CH₂)₃CH=CH₂ (ref. 25). Further characteristic broad absorptions are observed at ca. 3315 and 3400 cm⁻¹, which can be assigned to the NH as well as OH groups. The aldehyde functionalities present in 2 and 8 gave characteristic bands at 2732 and 2820 cm⁻¹ for the CH and at 1705 cm⁻¹ for the CO moieties. In addition, IR spectroscopy can be applied to monitor the progress of the hydroboration of 3 with [BH₃·SMe₂]⁺, since the νC–C vibration of the allylic units in the respective starting compounds (ca. 1630 cm⁻¹) disappears in the course of the reaction. After H₂O₂ treatment new bands for the terminal hydroxyl functionalities in 5a and 5b are found at ca. 3400 cm⁻¹, which is typical for primary alcohols. Solely broad absorptions are observed in the IR spectra; hydrogen-bridge formation and hence formation of molecular networks are the most obvious.

The ¹H and ¹³C{¹H} NMR spectra of all compounds are characterized by well-resolved resonance signals for the organic groups present (see the Experimental section). Most typical for aldehydes 2b,c and 8a–c is the resonance signal at 10.07 ppm. This functionality allows the monitoring of the progress of the appropriate porphyrin formation because this signal disappears during the course of the reaction. Further evidence for the successful formation of the porphyrins is the appearance of a singlet at 8.92 ppm, which can be assigned to the pyrrole hydrogen atoms. Also very distinctive is the resonance signal of the NH units at –2.8 ppm, while zincation leads to the disappearance of this signal and hence this unit can also be used to monitor the formation of the appropriate zinc porphyrins. Further indicative groups are the SiMe₃, Si(CH₂)₃Me, and Si(CH₂)₃CH=CH₂ entities (see the Experimental section). Particularly the latter group is best suited to study the progress of the consecutive hydroboration–oxidation processes since new resonances for the Si(CH₂)₃OH building blocks are found (see the Experimental section). Similar to the IR spectra, the representative resonance signals for the Si(CH₂)₃CH=CH₂ groups in 3b and 3c at ca. 2.0 (SiCH₃), 5.0 (H₂C=CH) and 6.0 ppm (CH=) in CDCl₃ disappear on hydroboration and after oxidation with H₂O₂, new signals can be found at 0.9 (SiCH₂CH₂CH₂OH), 1.7 (SiCH₂CH₂CH₂OH), 3.5 (SiCH₂CH₂CH₂OH) and 4.5 ppm (SiCH₂CH₂CH₂OH) for alcohols 5a and 5b in dmsol-d₄, respectively. Similar observations were made in the ¹³C{¹H} NMR spectroscopic studies (see the Experimental section).

Additionally, the ²⁹Si{¹H} NMR spectra of the carbosilane-based porphyrins 3b,c, 4a,b, 9b,c and 10a,b and the aldehydes 2b,c and 8b,c were measured. For example, the ²⁹Si{¹H} NMR spectra of 9 and 10 (in CDCl₃) show, as expected, two resonance signals at ca. –1.45 ppm and between –3.9 and –5.7 ppm, which can be assigned to the core and terminal silicon atoms (see the Experimental section). The values for the inner silicon atoms are in good agreement with tetraphenyl silane (–14.98 ppm).

ESI-TOF mass spectrometric studies were carried out for all aldehyde derivatives and the ⁰th generation porphyrins. Compounds 2c, 3b,c and 5a show the protonated molecular ion peak [M + H]⁺, while for 4a,b [M]⁺ is characteristic. Compounds 5b, 6a,b and 8a,c could successfully be ionized by doping with KSCN and hence the ion [M + K]⁺ could be detected (see the Experimental section).

UV-Vis absorption spectra were additionally recorded for porphyrins 3b,c, 4a,b, 5a,b, 6a,b, 9a–c and 10a–c, in order to analyze the effect of the dendritic branches on the optical properties of the porphyrin ring. The spectra were measured in CH₂Cl₂ and thf as solvents (Table 1). The porphyrin core of 3b shows one Soret band at 420 nm in CH₂Cl₂ and four Q bands at 517, 552, 592 and 648 nm (Fig. 1a). Metallation of 3b with zinc(II) did not influence the position of the Soret band (4a, 421 nm, in CH₂Cl₂) (Fig. 1b) but has a significant impact on the shape of the Q band pattern. Two characteristic bands at 549 and 588 nm are observed in CH₂Cl₂, which is typical for metallo-porphyrins. Fig. 1 also shows the difference between the UV-Vis spectra of the corresponding ⁰th and ¹st generation dendritic porphyrins. conspicuous is that the transitions typical for the ¹st generation dendritic porphyrins, for example, 9b, are nearly meeting the shape of the bands of the appropriate ⁰th generation systems, as, for example 3b, with just little enhancement of the band intensities and a very small red shift in the Soret band (Fig. 1a). Similar observations were made for zinc porphyrins 4a and 10b (Fig. 1b). The increasing shielding effect of growing dendrons around the porphyrin core as, for example, described by Aida and co-workers for an aryl ether scaffold³⁰ does not appear in the case of our systems. The reason therefore is apparent when looking at the molecular structure of the ¹st generation 9b (Fig. 10/11). Compared to aryl ether dendrons, the here reported aryl silyl dendrons (e.g. 9b) are more rigid. A back-folding, as observed for the aryl ether dendrons, is impossible and that implies that the porphyrin core plane is even in the ¹st generation type compounds easily accessible from above and below by solvents. A dendritic effect is therefore not observed by comparing the UV-Vis data of the ⁰th and ¹st generation molecules. The data correlate well with reported literature spectra for silyl-functionalized porphyrins.

X-ray investigations

Single crystals of 3b (as 3b·1/4CH₂Cl₂), 3c, 4a and 9b (as 9b·3.5EtOH) were grown by slow diffusion of CH₂Cl₂ into EtOH solutions containing the respective compounds, while single crystals of 6a (as 6a·2thf) were obtained by layering a thf solution containing 6a with pentane at ambient temperature. The molecular structures of 3b,c, 4a and 6a are displayed in Fig. 2,
In the case of 9b the asymmetric unit comprises two crystallographically independent centrosymmetric halves of 9b, denoted as 9bA and 9bB. Their molecular structures are depicted in Fig. 10 and 11. Crystal and intensity collection data of 3b·1/4CH2Cl2, 3c, 4a, 6a·2thf and 9b·3.5EtOH are summarized in Table S1,† while selected bond lengths and angles are given in Tables 2 and 3, respectively.

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As already mentioned for 9b, even 3c possesses in the solid state crystallographically imposed inversion symmetry, whereby the inversion centres are located in the middle of the atoms N2/N2A (3c, Fig. 6), N1/N1A (9bA, Fig. 10) and N4/N4A (9bB, Fig. 11). For all other crystallographically characterized porphyrins no crystallographically implied symmetry is observed, thus 3b·1/4CH2Cl2, 4a, and 6a·2thf are C1 symmetric in the solid state.

It should be emphasised that meso-tetraphenylporphyrins carrying at the para position any kind of Si-containing groups have been sparingly characterised by single crystal X-ray diffraction studies so far. The solid state structures of 5,10,15,20-tetrakis(4-pentamethyldisilanyl)phenyl)porphyrin32a and of 5,10,15,20-tetrakis[4-(diethoxymethylsilyl)phenyl]porphyrin 32b are already described in the literature.

However, experimentally observed bond lengths and angles for the end-grafted carbosilane branches of all functionalized meso-tetraphenylporphyrins described here are in agreement with parameters typically found for phenylene-based carbosilanes.24,33

The molecular structures of H2TPP(4-SiMe2(CH2CH=CH2))4 (3b) and its related zinc(ii) species Zn(ii)-TPP(4-SiMe2(CH2CH=CH2))4 (4a) in the solid state are depicted in
bond lengths and angles of the C20N4 cores of tallographically independent porphyrin molecule. Related
be regarded as structurally isomorphic to each other.
 solvent molecule of CH2Cl2 is observed in the crystal structure,
compared with 4a atoms only one atomic position is displayed. The sign - refers to calculated interplanar angles between terminal C6H4 groups
and the central C20N4H2 core.

Fig. 2 ORTEP diagram (50% ellipsoid probability) of the molecular structure of 3b. All C-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign - refers to calculated interplanar angles between terminal C6H4 groups and the central C20N4 core.

Fig. 3 ORTEP diagram (50% ellipsoid probability) of the molecular structure of 4a. All hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign - refers to calculated interplanar angles between terminal C6H4 groups and the central C20N4Zn core.

Fig. 2 and 3. Both porphyrins crystallize in the tetragonal space group P41 with similar dimensions of their respective unit cells (Table S11). For 3b a partially occupied packing solvent molecule of CH2Cl2 is observed in the crystal structure, which should be found for 4a as well. However, no electron density peaks of 4a could be used for the refinement of an analogous packing solvent molecule. Despite this, 3b and 4a can be regarded as structurally isomorphic to each other.

The asymmetric unit of both 3b and 4a possesses one crystallographically independent porphyrin molecule. Related bond lengths and angles of the C20N4 cores of 3b and 4a can be considered as identical to each other within standard deviations (Tables 2 and 3). Not surprisingly, the N⋯N distances of opposite nitrogen atoms of 3b are significantly longer, when compared with 4a (3B, N1⋯N3/N2⋯N4 = 4.160(5)/4.113(5) Å

Table 2. Selected bond lengths (Å) of 3b, 1/4CH2Cl2, 3c, 4a, 6a. 2thf and 9b. 3.5EtOH

| Bond Lengths (Å) | 3b, 1/4CH2Cl2 | 3c, 4a, 6a. 2thf | 9b, 3.5EtOH |
|------------------|---------------|-----------------|-------------|
| C1-C2            | 1.399(5)      | 1.411(5)        | 1.399(5)    |
| C2-C3            | 1.345(5)      | 1.404(4)        | 1.390(4)    |
| C3-C4            | 1.364(5)      | 1.411(5)        | 1.399(5)    |
| C4-C5            | 1.382(5)      | 1.408(5)        | 1.399(5)    |
| C5-C6            | 1.364(5)      | 1.406(5)        | 1.399(5)    |
| C6-C7            | 1.374(5)      | 1.403(4)        | 1.399(5)    |
| C7-C8            | 1.370(5)      | 1.400(4)        | 1.399(5)    |
| C8-C9            | 1.377(5)      | 1.405(4)        | 1.399(5)    |
| C9-C10           | 1.377(5)      | 1.405(4)        | 1.399(5)    |
| C10-C11          | 1.382(5)      | 1.408(5)        | 1.399(5)    |
| C11-C12          | 1.399(5)      | 1.411(5)        | 1.399(5)    |
| C12-C13          | 1.405(5)      | 1.414(5)        | 1.399(5)    |
| C13-C14          | 1.390(4)      | 1.400(4)        | 1.399(5)    |
| C14-C15          | 1.399(5)      | 1.411(5)        | 1.399(5)    |
| C15-C16          | 1.408(5)      | 1.414(5)        | 1.399(5)    |
| C16-C17          | 1.403(4)      | 1.400(4)        | 1.399(5)    |
| C17-C18          | 1.411(5)      | 1.404(4)        | 1.399(5)    |
| C18-C19          | 1.404(4)      | 1.399(5)        | 1.399(5)    |
| C19-C20          | 1.400(4)      | 1.399(5)        | 1.399(5)    |
| C20-C1           | 1.414(5)      | 1.414(5)        | 1.399(5)    |

Symmetry code: -x, y+1, -z+1. Symmetry code: x, -y, z.
Porphyrins 3b and 4a are structurally isomorphic to each other (vide supra) and consequently their crystal structures are identical. For both porphyrins a 3D network structure is observed in the solid state of which a selected part has been illustrated in Fig. 4 (3b) and Fig. 5 (4a). Thereby it is observed that all four crystallographically different C₆H₄ rings are involved in T-shaped π–π contacts with the respective C₂₀N₄ cores (Fig. 4 and 5). Geometrical features of these π–π contacts of 3b and 4a (Fig. 4 and 5) are in good agreement with each other, when comparing both molecules.

The molecular structure of H₃TPP(4-SiMe(CH₂CH₂=CH₂)₃)(3c) in the solid state is depicted in Fig. 6. The replacement of one methyl group of the carbosilane SiMe₃(CH₂CH₂=CH₂) moiety in 3b by an allyl unit, as characteristic for 3c, induces considerable changes. In contrast to 3b, porphyrin 3c crystallizes in the triclinic space group P1 with crystallographically imposed inversion symmetry. Thus, the asymmetric unit of 3c comprises just half of the molecule, while the second half is generated by an inversion center which is located at the crossing point of the atoms N1/N1A and N2/N2A (Fig. 3). Furthermore, it is astonishing to notice that related bond lengths of the C₂₀N₄ core of 3c, when compared with those of 3b and 4a and those of 6a and 9b as well, are significantly elongated (Table 2). As a wrongly determined space group may cause such deviations the structural refinement of 3c was checked with the utmost precision; however, there are no indications that the unit cell dimensions and space group of 3c are not accurate (Table S1†). For example, the N⋯N distances of opposite N atoms of 3c (N1⋯N1A/N2⋯N2A = 4.325(5)/4.228(5) Å) are by far the longest ones of the here described porphyrins (Table 2). A possible explanation of this unexpected observation for 3c might be drawn from the crystal structure of 3c, which is illustrated in Fig. 7. In contrast to the observation of 3D network structures for 3b and 4a (Fig. 4 and 6) which are induced by T-shaped π–π interactions, for 3c the formation of 2D layers has been noted. The 2D layers are formed along the crystallographic a- and b-axes, but not along the crystallographic c-axes as depicted in Fig S1 and S2.† Moreover, only the C₆H₄ aromatic group comprising the atoms C11 to C16 and symmetry generated analogues is involved in T-shaped π–π interactions with the C₂₀N₄ core of adjacent molecules.
Thereby, comparatively large centroid-to-centroid distances are observed (Fig. 7). To deduce that the different crystal structure of 3c is responsible for the observation of significantly different bond lengths of 3c, when compared to those of 3b and 4a, is certainly a more qualitative description. Hence, further work, e.g. quantum chemical calculations, is required to figure out the origin of this remarkable phenomenon.

The molecular structure of Zn(II)-TPP(4-SiMe2((CH2)3OH))4 (6a) is depicted in Fig. 8. Porphyrin 6a crystallizes in the triclinic system P1 with one molecule of 6a in the asymmetric unit cell. As indicated before, bond lengths and angles of the central C20N4 core of 6a compare well with those of 3b, 4a and 9b (Tables 2 and 3). Due to formation of an intermolecular O(H)–Zn bond (Zn1–O1 = 2.155(3) Å), the Zn(II) ion of 6a is significantly moved out of the basal plane into the direction of the coordinated O donor atom. Thus, the Zn1 atom is located 0.255(2) Å above the calculated mean plane of the atoms N1 to N4 (rmsd = 0.022 Å, hdp observed for N3 with 0.022(2) Å).

The exchange of the terminal allyl groups of 4a by 3-propoxy functionalities, as present in 6a, resulted in a completely different packing mode. There are no π–π interactions of any kind observed for 6a in the solid state. Instead, the crystal structure is exclusively governed by reciprocal formation of intermolecular O(H)–Zn contacts along the crystallographic a-axes together with formation of intermolecular O(H)⋯O hydrogen bonds along the crystallographic b-axes. Fig. S3 and Table S2† show bond lengths and angles for the characteristic intermolecular hydrogen bonds. A part of the thus formed 2D network is depicted in Fig. 9. Due to formation of intermolecular π–π interactions and the corresponding larger centroid-to-centroid distances, the porphyrin planes are not parallel any more, but they form a dihedral angle of 17° (Table S3†).

Fig. 4 Above: Graphical illustration of a selected part of the 3D network formed by 3b due to intermolecular π–π interactions. Labels A–C refer to a 1̅–3̅̅̅ symmetry generated molecule of 3b. All hydrogen atoms and terminal substituents at the silicon atoms are omitted for clarity. Below: graphical illustration of the four different types of intermolecular π–π interactions between the aromatic C6H4 groups with respective parts of the porphyrin core. The sign † refers to calculated interplanar angles between differently colored functionalities. Dotted lines indicate the shortest observed distances between the geometrical centroids of the C6H4 groups and the respective centroids/atoms of the porphyrin core with D1 = centroid of C21–C26, D3 = centroid of C27–C32, D4 = centroid of C33–C38, D6 = centroid of C39–C44, D2 = centroid of N1 and C2, D5 = centroid of C12–C14 and symmetry generated related atoms/fragments.
layers is furthermore graphically illustrated in Fig. 9. It is surprising to note that the formation of 1D chains, as a part of the 2D network structure, due to mutual intermolecular O(H)–Zn contacts as observed for 6a, has not been observed so far for any kind of O-functionalised metalloporphyrins possessing 3d transition metal ions. Related metalloporphyrins functionalised by any kind of O-donor atoms, with the oxygen atoms belonging to alcohol, ether, carbonic acid and/or carbonyl functionalities, form either dimers,35 trimers36 or polymeric 2D37 and 3D38 networks, respectively.

Porphyrin H2TPP(4-Si(C6H4-4-Si(CH2CH2)Me2)3)4 (9b) crystallises in the triclinic space group P1. The asymmetric unit contains half of two crystallographically independent molecules of 9b, denoted as 9bA and 9bB. Both 9bA and 9bB possess in the solid state crystallographically imposed inversion symmetry, whereby the molecular structures of both individual molecules are depicted in Fig. 10 and 11. The bond distances and angles of the C20N4 cores of 9bA and 9bB do not only compare well with each other, they can be even considered as closely related to analogous data reported here for 3b, 4a and 6a but not 3c (see above and Tables 2 and 3).

Due to the presence of sixteen crystallographically independent C6H4 aromatic rings of both 9bA and 9bB, determination of the crystal structure of 9b with respect to possible π–π interactions is rather complicated.39 However, it was found that a 3D network is formed by 9b in the solid state due to T-shaped...
π–π interactions. This 3D network can be understood as being formed of 2D layers of molecules of 9bA and 9bB of which a part is illustrated in Fig. 12. Further descriptions of the individual interactions are given in Fig. 14 and S4–S6.† The 2D layers interact then with each other by means of T-shaped π–π interactions exclusively between molecules of either 9bA or 9bB (Fig. 13). The respective π–π interactions being responsible for the formation of the 2D layers and of the 3D network are then separately illustrated in Fig. 14. The inter-layer distance between 2D layers corresponds to 25.1408 Å (=b), (Fig. 13).

Different types of non-planar distortions commonly observed for porphyrins have been already explicitly discussed. In the case of here structurally described porphyrins it can be determined that the central C20N4 porphyrin cores can be regarded as planar which can be concluded from, for example, the sum of angles around the 5,10,15,20-anellated atoms of the C20N4 cores (Table 3) and further data are given in Table S3 and Fig. S7,† including accompanying remarks.

In summary, the observation of the formation of 3D (3b, 4a and 9b) or 2D networks (3c) resulting from intermolecular
T-shaped π–π interactions is not a specific feature of the here reported porphyrins. There are already two crystallographically described meso-tetraphenylporphyrins known bearing terminal Si-functionalities at the para-position of the phenyl rings, namely 5,10,15,20-tetrakis(4-pentamethyldisilany1)phenyl)porphyrin and 5,10,15,20-tetrakis[4-(diethoxymethylsilyl)]phenyl]porphyrin, which can be regarded as closely related to the here reported porphyrins. Bond lengths and angles of the C_{20}N_{4} porphyrin cores of these two reported samples are in very good agreement with the corresponding data observed for 3b, 4a, 6a and 9b, respectively.

Especially for 5,10,15,20-tetrakis[4-(diethoxymethylsilyl)]phenyl]porphyrin it is indicated that “no significant short contacts such as π-stacking” could be observed, which is attributed to the steric hindrance of the terminal silyl functionalities. It seems, however, likely, that only sandwich type π–π interactions have been ruled out.

In the discussion of the crystal structures of Zn(TPP) and Ag(TPP), which are isomorphous to H_{2}TPP, T-shaped π–π interactions have been explicitly mentioned. Interplanar angles between interacting aromatic units are given, although no centroid-to-centroid distances and the final type of assemblies formed have been mentioned. In the case of a report on the crystallographic characterisation of Fe(TPP) as a toluene solvate, the formation of 1D chains, due to sandwich type π–π interactions, is observed. One can thus assume that for non-functionalised M(TPP) (M = 3d metal ion) type porphyrins, especially for those in which the central metal ion is not coordinated by one and/or two donor molecules, π–π interactions play a significant role in the crystal structures. Indeed, for

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**Fig. 8** ORTEP diagram (50% ellipsoid probability) of the molecular structure of 6a. All C-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign refers to the calculated interplanar angles between terminal C_{6}H_{4} groups and the central C_{20}N_{4}Zn core.

**Fig. 9** Graphical representation of a part of one of the 2D layers formed by 6a in the solid state due to formation of intermolecular O–H⋯O hydrogen bonds and O(H)⋯Zn bonds. All C-bonded hydrogen atoms and packing solvent molecules are omitted for clarity. Of disordered atoms only one atomic position is displayed. Labels A–E refer to a 1<sup>st</sup>–5<sup>th</sup> symmetry generated molecule of 6a.
Zn(TPP), being co-crystallized with different guest molecules, a review by Byrn et al.\textsuperscript{44} for over 200 different cases mentions explicitly the observation of intermolecular T-shaped π–π interactions, although no geometrical features or types of assemblies were given.

**Conclusions**

The preparation of a series of 0\textsuperscript{th} and 1\textsuperscript{st} generation carbo-silane dendrimer-based porphyrins of types H\textsubscript{2}TPP(4-SiRR′Me)\textsubscript{4}, Zn(II)-TPP(4-SiRR′Me)\textsubscript{4} (R = R′ = Me, CH\textsubscript{2}CH=CH\textsubscript{2},...

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**Fig. 10** ORTEP diagram (20% ellipsoid probability) of the molecular structure of 9bA. All carbon-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign ‘-’ refers to the calculated interplanar angles between the directly porphyrin bonded C\textsubscript{6}H\textsubscript{4} groups and the central C\textsubscript{20}N\textsubscript{4}H\textsubscript{2} core. Symmetry code for A: -x + 2, -y, -z.

**Fig. 11** ORTEP diagram (20% ellipsoid probability) of the molecular structure of 9bB. All carbon-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign ‘-’ refers to the calculated interplanar angles between the directly porphyrin bonded C\textsubscript{6}H\textsubscript{4} groups and the central C\textsubscript{20}N\textsubscript{4}H\textsubscript{2} core. Symmetry code for A: -x + 1, -y and for #:, -z + 1.\textsuperscript{43a}
CH₂CH₂CH₂OH; R = Me, R′ = CH₂CH₂CH₂OH; TPP = tetraphenyl porphyrin), H₂TPP[4-Si(C₆H₄-1,4-SiRR′Me)₃]₄, and Zn(n)TPP[4-Si(C₆H₄-1,4-SiRR′Me)₃]₄ (R = R′ = Me, CH₂CH₂CH₂; R = Me, R′ = CH₂CH₂CH₂) using the Lindsey condensation methodology is described. Functionalization of TPP with the carbosilane dendrons leads to a slight bathochromic shift of the Soret and Q bands in the UV-Vis spectra, which is in agreement with the literature. The structures of five samples (3b,c, 4a, 6a, 9b) in the solid state have been determined by single X-ray structure determination. The supramolecular structures of the allyl 0th generation species 3b,c, 4a and the 1st generation carbosilane-containing porphyrin 9b are primarily controlled by π-π interactions, while in the hydroxyl-functionalized porphyrin 6a the network formation is exclusively set by zinc-oxygen coordination and hydrogen bonding intermolecular interactions. Conspicuously, porphyrin 3b and its analogous zinc-metallated system 4a possess an identical 3D supramolecular structure as both compounds...
can be regarded as isomorphic in the solid state. On the other hand, the eight allyl groups in 3c, instead of the four allyl units present in 3b, modify the 3D network into a 2D network which might be responsible for the observation of significantly larger bond lengths of its C20N4 core in comparison with the related bond lengths of the other here described porphyrins.

For meso-tetraphenylporphyrins bearing any kind of substituent at the phenyl rings it seems less likely that intermolecular sandwich type $\pi-\pi$ interactions can be observed, although T-shaped $\pi-\pi$ interactions might be found. For such cases we do not find, to the best of our knowledge, precise comments for crystallographically described representatives. We assume, however, that especially T-shaped $\pi-\pi$ interactions should be observed, as reported here for 3b, 3c, 4a and 9b, at least in such cases where the central metal ions are not coordinated by additional donor solvents or the two N(H)-protons of the central porphyrin rings are not involved in hydrogen bridges with protic donor solvents.

**Experimental section**

**General data**

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, toluene and 2-pentane were purified by distillation from sodium–benzophenone ketyl; CH2Cl2 and CHCl3 were purified by distillation from calcium hydride. Diethylamine and diisopropylamine were distilled from KOH; absolute MeOH was obtained by distillation from magnesium.

**Instrumentation**

Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer Spectrum 1000 ($\tilde{v}$ in cm$^{-1}$). UV-Vis spectra were measured with a Thermo Electron Corporation Genesys 6 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer ($^1$H NMR at 250.12 MHz and $^{13}$C{$^1$H} NMR at 62.86 MHz) in the Fourier transform mode. Chemical shifts are reported in $\delta$ units (parts per million) downfield from tetramethylsilane ($\delta = 0.00$ ppm) with the solvent as the reference signal (CDCl3: $^1$H NMR, $\delta = 7.26$; $^{13}$C{$^1$H} NMR, $\delta = 77.16$; DMSO-d$_6$: $^1$H NMR, $\delta = 2.54$; $^{13}$C{$^1$H} NMR, $\delta = 40.45$; thf-d$_8$: $^1$H NMR, $\delta = 1.72$; $^{13}$C{$^1$H} NMR, $\delta = 24.45$). The atom numbering is depicted in the ESI (Fig. S8†). The assignment of $^{13}$C{$^1$H} and $^{29}$Si{$^1$H} NMR spectroscopic signals is mainly based on $^{13}$C-DEPT-135 spectra and 2D-correlation spectra (gradient with sensitivity-enhanced heteronuclear multiple quantum correlation (gs-HMQC) for carbon and silicon and gradient with sensitivity-enhanced heteronuclear multiple bond correlation (gs-HMBC) for carbon). Please note that the resonance signal for the pyrrole-$\alpha$-C unit could only be detected for the zinc complexes under the measurement conditions applied. ESI-TOF mass spectra were recorded using a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Microanalyses were performed with a Thermo FlashAE 1112 instrument. Melting points of pure samples were measured with Gallenkamp MFB 595 010 equipment.

**Reagents**

1a, 2a, 3a,$^{21}$ 1b,$^{22}$ 1c, 7a,c,$^{24}$ 2b$^{23}$ and 7b, 8b, 9b$^{18a}$ were prepared according to published procedures. All other chemicals

Fig. 14 Graphical illustration of the respective T-shaped $\pi-\pi$ interactions observed in the solid state structure of 9b being responsible for the formation of 2D layers (left and middle) and for the interaction of 2D layers to give a 3D network.$^{40b}$
were purchased from commercial suppliers and were used as received.

**4-Diallylmethylsilylbenzaldehyde (2c)**

BuLi (1.7 M, 34.7 mmol, 20.4 mL, pentane) was added drop-wise to a Et2O (75 mL) solution containing 1c (17.37 mmol, 4.88 g) at −78 °C. After 1 h of stirring at this temperature the resulting solution was drop-wise transferred via a cannula to dimethyl formamide (52.12 mmol, 3.81 g, 4.04 mL) in tthf (50 mL) at 0 °C and the obtained reaction mixture was kept at this temperature for 15 min. Afterwards, it was warmed to ambient temperature, stirring was continued for 2 h, and then it was quenched with aqueous HCl (3 N, 80 mL). The obtained residue was extracted with Et2O (100 mL) and then with water (3 × 100 mL). The organic layer was filtered through a pad of silica gel and afterwards all volatiles were removed in oil-pump vacuum. The crude product was purified by column chromatography (a) \( ^{13} \)hexane, (b) 20 vol% CH\(_2\)Cl\(_2\)-hexane to afford 2c as colorless oil (14.86 mmol, 3.42 g, 86% based on 1c).

IR (film): \( \tilde{\nu} \) = 3074, 3024, 2992, 2911, 2880, 1627 (w, C=H), 1575, 1454, 1378 (m, CH\(_3\) bending), 836, 811, 796 (s, SiC). \( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = 8.90 (s, 8 H, H\(_{1}\)), 7.92 (brd, \( J_{HH} = 7.9 \) Hz, 8 H, H\(_{5}\)), 6.04 (ddt, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 10.1 \) Hz, 8 H, H\(_{10}\)), 5.10 (ddt, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 0.9 \) Hz, 8 H, cis-H\(_{11}\)), 5.06 (ddt, \( J_{HH} = 10.1 \) Hz, \( J_{HH} = 2.0 \) Hz, \( J_{HH} = 0.9 \) Hz, 8 H, trans-H\(_{11}\)), 2.10 (ddt, \( J_{HH} = 8.0 \) Hz, \( J_{HH} = 0.9 \) Hz, 32 H, H\(_{9}\)), 0.58 (s, 24 H, H\(_{8}\)), \( -2.69 \) (brs, 2 H, NH), cis-H\(_{12}\)). \( ^{13} \)C\( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = 142.9 (4 C\(_{4}\)), 136.1 (4 C\(_{8}\)), 134.3 (8 C\(_{10}\)), 132.3 (8 C\(_{10}\)), 131.1 (br, 8 C\(_{10}\)), 120.1 (4 C\(_{8}\)), 114.1 (8 C\(_{10}\)), 21.8 (8 C\(_{10}\)), \(-5.6 \) (4 C\(_{4}\)). 29Si\( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = -5.2. ESI-TOF: \( m/z \) = 1111.50 [M + H\(^{+}\)] (calcd 1111.54). Anal. calcld for C\(_{72}\)H\(_{78}\)N\(_{4}\)Si\(_{4}\): C, 76.29; H, 7.00; N, 5.56. Found: C, 76.03; H, 7.26; N, 5.30.

**meso-Tetrasakis(4-diallylmethylsilylphenyl)porphyrin (3c)**

To aldehyde 2c (10.00 mmol, 2.30 g) and pyrrole (10.00 mmol, 0.671 g, 0.69 mL) dissolved in CH\(_{2}\)Cl\(_{2}\) (1000 mL) [BF\(_{3}\)-Et\(_{2}\)O] (1.00 mmol, 0.142 g, 0.13 mL) was added in a single portion. The reaction solution was stirred for 2 h and then 2,3-dichloro-5,6-dicyano-benzonitrile (7.50 mmol, 1.70 g) was added in a single portion and stirring was continued for 1 h. The reaction mixture was washed with saturated NaHCO\(_{3}\) (100 mL) and then with water (3 × 100 mL). The organic layer was filtered through a pad of silica gel and afterwards all volatiles were removed in oil-pump vacuum. The crude product was purified by column chromatography (a) \( ^{13} \)hexane and (b) 20 vol% CH\(_{2}\)Cl\(_{2}\)-hexane. Porphyrin 3c was obtained as a dark red solid (0.69 mmol, 0.76 g, 27% based on 2c).

Mp = 350 °C (dec). IR (KBr disc): \( \tilde{\nu} \) = 3314 (s, NH), 3070, 3006, 2994, 2966, 2912, 2880, 1628 (m, C=C), 1250 (m, CH\(_{2}\) bending), 800 (s, SiC). \( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = 8.90 (s, 8 H, H\(_{1}\)), 8.26 (brd, \( J_{HH} = 7.9 \) Hz, 8 H, H\(_{5}\)), 7.92 (brd, \( J_{HH} = 7.9 \) Hz, 8 H, H\(_{6}\)), 6.04 (ddt, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 10.1 \) Hz, 8 H, H\(_{10}\)), 5.10 (ddt, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 0.9 \) Hz, 8 H, cis-H\(_{11}\)), 5.06 (ddt, \( J_{HH} = 10.1 \) Hz, \( J_{HH} = 2.0 \) Hz, \( J_{HH} = 0.9 \) Hz, 8 H, trans-H\(_{11}\)), 2.10 (ddt, \( J_{HH} = 8.0 \) Hz, \( J_{HH} = 0.9 \) Hz, 32 H, H\(_{9}\)), 0.58 (s, 24 H, H\(_{8}\)), \(-2.69 \) (brs, 2 H, NH), cis-H\(_{12}\)). \( ^{13} \)C\( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = 142.9 (4 C\(_{4}\)), 136.1 (4 C\(_{8}\)), 134.3 (8 C\(_{10}\)), 134.1 (8 C\(_{10}\)), 132.3 (8 C\(_{10}\)), 131.1 (br, 8 C\(_{10}\)), 120.1 (4 C\(_{8}\)), 114.1 (8 C\(_{10}\)), 21.8 (8 C\(_{10}\)), \(-5.6 \) (4 C\(_{4}\)). 29Si\( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = -5.2. ESI-TOF: \( m/z \) = 1111.50 [M + H\(^{+}\)] (calcd 1111.54). Anal. calcld for C\(_{72}\)H\(_{78}\)N\(_{4}\)Si\(_{4}\): C, 77.78; H, 7.07; N, 5.04. Found: C, 77.68; H, 6.59; N, 4.80.

**meso-Tetrasakis(4-alloyldimethylsilylphenyl)porphyrin zinc (4a)**

To 3b (0.050 mmol, 0.0504 g) dissolved in CHCl\(_{3}\) (15 mL), a MeOH solution (10 mL) containing [Zn(OAc)\(_{2}\)-2H\(_{2}\)O] (0.100 mmol, 0.0219 g) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and then was washed with saturated NaHCO\(_{3}\) (15 mL) followed by washing with water (2 × 15 mL). The organic layer was dried over Na\(_{2}\)SO\(_{4}\). All volatiles were removed in oil-pump vacuum to afford 4a as a dark red solid (0.495 mmol, 0.053 g, 99% based on 3b).

Mp = 350 °C (dec). IR (KBr disc): \( \tilde{\nu} \) = 3055, 3011, 2989, 2911, 2954, 2908, 2878, 1627 (w, C=C), 125 (m, CH\(_{2}\) bending), 836, 820, 811, 796 (s, SiC). \( ^{1} \)H NMR (CDCl\(_{3}\)): \( \delta \) = 9.00 (s, 8 H, H\(_{1}\)), 8.25 (brd, \( J_{HH} = 7.9 \) Hz, 8 H, H\(_{5}\)), 7.90 (brd, \( J_{HH} = 7.9 \) Hz, 8 H, H\(_{6}\)), 6.02 (ddt, \( J_{HH} = 17.0 \) Hz, \( J_{HH} = 10.1 \) Hz, \( J_{HH} = 8.1 \) Hz, 4 H, cis-H\(_{11}\)).
H\(^{10}\), 5.05 (brd, \(J_{HH} = 17.0 \) Hz, 4 H, \(cis\)-H\(^{11}\)), 5.02 (brd, \(J_{HH} = 10.1 \) Hz, 4 H, \(trans\)-H\(^{11}\)), 2.03 (brd, \(J_{HH} = 8.1 \) Hz, 8 H, H\(^3\)), 0.56 (s, 24 H, H\(^4\)). \(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\)): \(\delta = 150.2 \) (4 C\(_4\)), 143.4 (4 C\(_4\)), 137.5 (4 C\(_4\)), 134.8 (4 C\(_4\)), 133.9 (8 C\(_8\)), 132.1 (8 C\(_8\)), 131.8 (8 C\(_8\)), 121.2 (4 C\(_4\)), 113.6 (4 C\(_4\)), 24.0 (4 C\(_4\)), −3.2 (8 C\(_8\)).

\(^{29}\)Si\(^{1}\)H NMR (CDCl\(_3\)): \(\delta = −4.1 \) (4 Si). ESI-TOF: \(m/z = 1070.44 \) [M]\(^+\) (calculated 1070.40). Analyzed for C\(_{64}\)H\(_{70}\)N\(_4\)Si\(_4\)Zn (1073.00): C, 71.64; H, 6.58; N, 4.22. Found: C, 71.44; H, 6.58; N, 4.98.

**meso-Tetakis[4-(diallylmethylsilyl)phenyl]porphyrinato zinc (4b)**

To porphyrin 3c (0.050 mmol, 0.056 g) dissolved in CHCl\(_3\) (15 mL), [Zn(OAc)\(_2\)]-2H\(_2\)O (0.100 mmol, 0.0219 g) dissolved in MeOH (10 mL) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and afterwards it was washed with saturated NaHCO\(_3\) (15 mL) and then with water (2 × 15 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and all volatiles were removed in oil-pump vacuum to afford 4b as a dark red solid (0.490 mmol, 0.0576 g, 98% based on 3c).

\(\text{Mp} = 350^\circ\text{C} \) (dec). IR (KBr disc): \(\tilde{\nu} = 3070, 3056, 3008, 2990, 2966, 2952, 2912, 2876, 1628 \) (m, C=C), 1252 (m, S\(_2\)C\(_6\)-bending), 820 (s, SIC), 798 (s, SIC). \(^{1}\)H NMR (CDCl\(_3\)): \(\delta = 8.98 \) (s, 8 H, H\(^1\)), 8.24 (brd, \(J_{HH} = 7.9 \) Hz, 8 H, H\(^1\)), 7.89 (brd, \(J_{HH} = 7.9 \) Hz, 8 H, H\(^1\)), 6.01 (ddt, \(J_{HH} = 17.0 \) Hz, \(J_{HH} = 10.1 \) Hz, \(J_{HH} = 8.1 \) Hz, 8 H, H\(^1\)), 5.07 (ddt, \(J_{HH} = 17.0 \) Hz, \(J_{HH} = 2.0 \) Hz, \(J_{HH} = 0.9 \) Hz, 4 H, cis-H\(^{11}\)), 5.03 (ddt, \(J_{HH} = 10.1 \) Hz, \(J_{HH} = 2.0 \) Hz, \(J_{HH} = 0.9 \) Hz, 4 H, trans-H\(^{11}\)), 2.02 (dt, \(J_{HH} = 8.1 \) Hz, \(J_{HH} = 0.9 \) Hz, 16 H, H\(^6\)), 0.55 (s, 12 H, H\(^9\)). \(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\)): \(\delta = 150.1 \) (4 C\(_4\)), 143.6 (4 C\(_4\)), 135.8 (4 C\(_4\)), 134.3 (8 C\(_8\)), 132.2 (8 C\(_8\)), 123.2 (8 C\(_8\)), 121.1 (4 C\(_4\)), 114.1 (8 C\(_8\)), 21.9 (8 C\(_8\)), −5.6 (4 C\(_8\)). ESI-TOF: \(m/z = 1174.48 \) [M]\(^+\) (calculated 1174.46). Analyzed for C\(_{72}\)H\(_{94}\)N\(_4\)O\(_8\)Si\(_4\)·H\(_2\)O (1273.90): C, 67.88; H, 7.60; N, 4.40. Found: C, 73.24; H, 6.45; N, 4.68.

**meso-Tetakis[4-methyl(3-hydroxypropyl)silylphenyl]-porphyrinato zinc (5a)**

To [BH\(_3\)·SMe\(_2\)] (2.0 M, 2.00 mmol, 1.00 mL) dissolved in thf (5.0 mL), porphyrin 3c (0.207 mmol, 0.230 g) in thf (30 mL) was added drop-wise over 10 min at 0°C. After 2 h of stirring at this temperature aqueous NaOH (3 M, 0.75 mL) was added and stirring was continued for 15 min. Afterwards, H\(_2\)O\(_2\) (30%, 0.75 mL) was added in a single portion and the appropriate reaction mixture was stirred at ambient temperature for 30 min. It was extracted with saturated aqueous K\(_2\)CO\(_3\) (20 mL) and then with a Et\(_2\)O-thf mixture (ratio 1:1, v/v; 50 mL). The organic layer was washed with water and filtered through silica gel (thf, column size 1 × 10 cm). All volatiles were removed in oil-pump vacuum and the residue was washed with Et\(_2\)O (3 × 15 mL) and then dried in oil-pump vacuum to give 5a as a dark red solid (0.150 mmol, 0.186 g, 72% based on 3c).

\(\text{Mp} = 350^\circ\text{C} \) (dec). IR (KBr disc): \(\tilde{\nu} = 3393 \) (s, OH), 3314 (s, NH), 3055, 3011, 2994, 2927, 2863, 1251 (m, CH\(_3\)-bending), 801 (s, SIC). \(^{1}\)H NMR (dmsod-d\(_2\)): \(\delta = 8.87 \) (s, 8 H, H\(^1\)), 8.26 (d, \(J_{HH} = 7.5 \) Hz, 8 H, H\(^8\)), 7.97 (d, \(J_{HH} = 7.5 \) Hz, 8 H, H\(^8\)), 4.56 (t, \(J_{HH} = 5.3 \) Hz, 8 H, OH)), 3.51 (t, \(J_{HH} = 6.2 \) Hz, 8 H, H\(^1\)), 1.67 (m, 8 H, H\(^8\)), 0.96 (m, 8 H, H\(^8\)), 0.50 (s, 24 H, H\(^4\)). \(^{13}\)C\(^{1}\)H NMR (thf-d\(_2\)): \(\delta = 143.5 \) (4 C\(_4\)), 138.6 (4 C\(_4\)), 134.8 (8 C\(_8\)), 133.1 (8 C\(_8\)), 131.7 (br, 8 C\(_4\)), 121.0 (4 C\(_4\)), 65.6 (4 C\(_1\)), 28.5 (4 C\(_1\)), 12.5 (4 C\(_4\)), −2.8 (8 C\(_8\)). ESI-TOF: \(m/z = 1293.70 \) [M + K]\(^+\) (calculated 1293.58). Analyzed for C\(_{72}\)H\(_{94}\)N\(_4\)O\(_8\)Si\(_4\)-thf (1273.90): C, 76.88; H, 7.60; N, 4.40. Found: C, 76.68; H, 7.65; N, 4.31.

**meso-Tetakis[4-dimethyl(3-hydroxypropyl)silylphenyl]-porphyrinato zinc (6a)**

To 5a (0.0926 mmol, 0.100 g) dissolved in thf (30 mL) a solution of [Zn(OAc)\(_2\)-2H\(_2\)O] (0.185 mmol, 0.0407 g) in MeOH (10 mL) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and afterwards was concentrated in oil-pump vacuum to dryness. The residue was dissolved in thf (20 mL) and filtered through a pad of silica gel.
(thf) and then all volatiles were removed in oil-pump vacuum. The remaining solid was washed with a Et₂O:pentane mixture (ratio 1:4 v/v,30 mL) and then dried in oil-pump vacuum to give the title compound as a dark red solid (0.0857 mmol, 0.0990 g, 93% based on 5a).

Mp = 350 °C (dec). IR (KBr disc): 8 = 3398 (m, OH), 3048, 3004, 2945, 2927, 2863, 1246 (s, CH₃ bending), 831, 798 (s, SiC). **¹H NMR (dmso-d₆): δ = 8.76 (s, 8 H, H³), 8.16 (d, J_HH = 7.1 Hz, 8 H, H₴), 7.89 (d, J_HH = 7.3 Hz, 8 H, H²), 4.49 (t, J_HH = 6.2 Hz, 4 H, OH), 3.46 (q, J_HH = 6.3 Hz, 8 H, H⁵), 1.63 (m, 8 H, H¹), 0.92 (m, 8 H, H²), 0.47 (s, 24 H, H³). **¹³C{¹H} NMR (dmso-d₆): δ = 150.4 (4 C), 144.2 (4 C), 138.6 (4 C), 134.7 (8 C), 132.6 (8 C and 8 C), 121.2 (4 C), 64.8 (4 C), 28.2 (4 C), 12.4 (4 C), −1.8 (8 C). **²⁹Si{¹H} NMR (dmso-d₆): δ = −2.1. ESI-TOF: m/z = 1179.50 [M + K⁺] (calced 1179.39). Anal. calc. for C₆₃H₇₆N₄O₄Si₄Zn (1143.04): C, 67.25; H, 6.70; N, 4.90. Found: C, 67.44; H, 7.12; N, 4.81.

**meso-Tetrakis[4-methylidin(3-hydroxypropyl)silylphenyl]-porphinor zinc (6b)**

To porphyrin 5b (0.0805 mmol, 0.100 g) dissolved in thf (30 mL), [Zn(OAc)₂·2H₂O] (0.1611 mmol, 0.03536 g) in MeOH (10 mL) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and afterwards all volatiles were removed in oil-pump vacuum. The obtained residue was dissolved in thf (50 mL) and filtered through a pad of silica gel (thf). All volatiles were removed in oil-pump vacuum. The remaining residue was washed with Et₂O (30 mL) and then dried in oil-pump vacuum to give 6b as a red solid (0.068 mmol, 0.089 g, 85% based on 5b).

**meso-Tetrakis[4-(diallylmethylsilylphenyl)silyl]benzaldehyde (8c)**

The same procedure as described for preparing 2b was applied in the synthesis of 8c (see above): BuLi (1.7 M, 6.00 mmol, 3.60 mL, 3pentane), 7e (3.00 mmol, 2.361 g) in Et₂O (40 mL), dimethyl formamide (9.00 mmol, 0.658 g, 0.70 mL) in thf (20 mL) and aqueous HCl (3 N, 25 mL). After appropriate work-up, 8c was isolated as colorless oil (2.46 mmol, 1.81 g, 82% based on 7e).

IR (film): 8 = 3074, 3050, 2996, 2969, 2913, 2878, 2819 (w, CHO), 2725 (w, CHO), 1705 (s, C=O), 1629 (w, C=C), 1252 (w, CH₃ bending), 1132, 821 (s, SiC), 802 (s, SiC). **¹H NMR (CDCl₃):** δ = 10.07 (s, 1 H, CHO), 7.89 (brd, J_HH = 8.1 Hz, 2 H, H²), 7.77 (brd, J_HH = 8.1 Hz, 2 H, H¹), 7.55 (brs, 12 H, H₇ and H₈), 5.80 (ddtt, J_HH = 16.9 Hz, J_HH = 10.2 Hz, J_HH = 8.0 Hz, 8 H, H¹). **¹³C{¹H} NMR (CDCl₃):** δ = 192.5 (1 C), 142.8 (1 C), 139.1 (3 C), 137.0 (1 C), 136.9 (2 C), 135.4 (6 C), 134.0 (6 C), 133.9 (3 C), 133.4 (6 C), 128.6 (2 C), 113.5 (6 C), 23.5 (6 C), −3.6 (3 C). **²⁹Si{¹H} NMR (CDCl₃):** δ = −14.7 (1 Si), −5.7 (3 Si). ESI-TOF: m/z = 775.01 [M + K⁺] (calced 775.30). Anal. calc. for C₆₃H₇₆O₄Si₄ (737.28): C, 74.94; H, 7.66. Found: C, 74.93; H, 7.77.

**meso-Tetrakis[4-tris(4-trimethylsilylphenyl)silyl]phenyl]-porphinor (9a)**

To 8a (4.00 mmol, 2.324 g) and pyrrole (4.00 mmol, 0.268 g, 0.28 mL) dissolved in CH₂Cl₂ (400 mL), [BF₃·OEt₂] (0.400 mmol, 0.057 g, 0.05 mL) was added in a single portion. The reaction solution was stirred for 2 h and then 2,3-dichloro-5,6-dicyanobenzoxadine (3.00 mmol, 0.681 g) was added in a single portion and stirring was continued for 1 h. The reaction mixture was washed with saturated NaHCO₃ (40 mL) and afterwards with water (3 × 40 mL). The organic layer was filtered through a pad of silica gel and then all volatiles were removed in oil-pump vacuum. The crude product was purified by column chromatography (a) “hexane and (b) 20 vol% CH₂Cl₂“hexane. After all volatiles were removed in oil pump vacuum, porphinor 9a was obtained as a dark red solid (0.256 mmol, 0.643 g, 26% based on 8a).

Mp = 350 °C (dec). IR (KBr disc): 8 = 3315 (s, NH), 3047, 2995, 2952, 2932, 2894, 1249 (m, CH₃ bending), 1133, 847 (s, SiC), 839 (s, SiC), 803. **¹H NMR (CDCl₃):** δ = 8.94 (s, 8 H, H²), 8.27 (brd, J_HH = 8.0 Hz, 8 H, H³), 8.02 (brd, J_HH = 8.0 Hz, 8 H, H⁴), 7.85 (brd, J_HH = 8.0 Hz, 24 H, H⁵), 7.70 (brd, J_HH = 8.0 Hz, 24 H, H⁶), 0.36 (s, 108 H, H₁₀), −2.72 (br, 2 H, NH). **¹³C{¹H} NMR (CDCl₃):** δ = 143.3 (4 C), 142.2 (12 C), 135.8 (24 C), 134.7 (8 C), 134.6 (12 C), 133.5 (4 C) 132.9
(24 C), 120.1 (4 C), −1.1 (36 C). 29Si[1H] NMR (CDCl3): δ = −14.2 (4 Si), −4.5 (12 Si). Anal. calc'd for C152H180N4Si16Zn·EtOH (3153.39): C, 72.17; H, 7.10; N, 1.67. Found: C, 72.49; H, 7.30, N, 1.88. Found: C, 72.17; H, 7.10; N, 1.67.

**meso-Tetrakis[4-tris(4-diallylmethylsilylphenyl)silyl]phenyl]-porphyrinato zinc (10a)**

To 9a (0.0139 mmol, 0.0350 g) in CHCl3 (5 mL), [Zn(OAc)2·2H2O] (0.0347 mmol, 0.0076 g) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and afterwards all volatiles were removed in oil-pump vacuum. The residue was extracted with CHCl3 (10 mL) and then with water (5 mL). The organic layer was dried over MgSO4 and all volatiles were removed in oil-pump vacuum to afford 10a as a dark red solid (0.0135 mmol, 0.340 g, 97% based on 9a).

Mp = 350 °C (dec). IR (KBr disc): ν = 3074, 3047, 2994, 2953, 2912, 1628 (m, C=C), 1249 (m, CH2 bending), 1132, 835 (s, SiC), 799 (s, SiC). 1H NMR (CDCl3): δ = 9.05 (s, 8 H, H1), 8.29 (brd, JHH = 8.0 Hz, 8 H, H2), 7.97 (brd, JHH = 8.0 Hz, 8 H, H3), 7.85 (brd, JHH = 8.0 Hz, 24 H, H4), 7.70 (brd, JHH = 8.0 Hz, 24 H, H5), 5.88 (ddt, JHH = 16.9 Hz, JHH = 10.2 Hz, JHH = 1.1 Hz, 24 H, H14), 4.95 (dt, JHH = 16.9 Hz, JHH = 21.1 Hz, JHH = 1.1 Hz, trans-H5), 4.92 (ddt, JHH = 10.2 Hz, JJH = 21.1 Hz, JHH = 1.1 Hz, trans-H5), 1.86 (dt, JHH = 8.1 Hz, JHH = 1.1 Hz, 24 H, H13), 0.38 (s, 72 H, H11). 13C{1H} NMR (CDCl3): δ = 150.1 (8 C), 144.0 (4 C), 140.4 (4 C), 135.8 (12 C13), 134.9 (12 C6), 134.6 (12 C4 and 8 C6), 134.1 (8 C1), 133.2 (4 C1), 133.0 (4 C4), 132.1 (8 C1), 131.5 (12 C12), 23.6 (12 C12), −3.5 (24 C). 29Si[1H] NMR (CDCl3): δ = −14.2 (4 Si), −4.5 (12 Si). Anal. calc'd for C172H230N4Si16Zn2EtOH (3982.26): C, 72.49; H, 7.30, N, 1.88. Found: C, 72.17; H, 7.10; N, 1.67.

**meso-Tetrakis[4-tris(4-diallylmethylsilylphenyl)silyl]phenyl]-porphyrinato zinc (10c)**

To 9c (0.0317 mmol, 0.100 g) in CHCl3 (15 mL), a solution of [Zn(OAc)2·2H2O] (0.0793 mmol, 0.017 g) in MeOH (5 mL) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and afterwards all volatiles were removed in oil-pump vacuum. The residue was extracted with CHCl3 (20 mL) and then with water (10 mL). The organic layer was dried over MgSO4 and all volatiles were removed in oil-pump vacuum to afford 10c as a dark red solid (0.0308 mmol, 0.099 g, 97% based on 9c).

Mp = 350 °C (dec). IR (KBr disc): ν = 3074, 3050, 2994, 2968, 2912, 2878, 1628 (m, C=C), 1249 (m, CH2 bending), 1132, 820 (s, SiC), 802 (s, SiC). 1H NMR (CDCl3): δ = 9.03 (s, 8 H, H1), 8.27 (brd, JHH = 8.0 Hz, 8 H, H2), 7.97 (brd, JHH = 8.0 Hz, 8 H, H3), 7.82 (brd, JHH = 8.0 Hz, 24 H, H4), 7.67 (brd, JHH = 8.0 Hz, 24 H, H5), 5.85 (ddt, JHH = 16.9 Hz, JHH = 9.6 Hz, JHH = 8.1 Hz, 24 H, H14), 4.94 (ddt, JHH = 16.9 Hz, JHH = 21.1 Hz, JHH = 1.1 Hz, trans-H5), 4.92 (ddt, JHH = 10.2 Hz, JJH = 21.1 Hz, JHH = 1.1 Hz, trans-H5), 1.89 (dt, JHH = 8.1 Hz, JHH = 8.1 Hz, 48 H, H13), 0.36 (s, 36 H, H11). 13C{1H} NMR (CDCl3): δ = 150.1 (8 C1), 144.1 (4 C), 138.8 (12 C13), 135.7 (24 C14), 135.1 (12 C12), 134.6 (8 C), 134.2 (4 C1), 133.4 (12 C1), 133.0 (4 C4), 132.9 (4 C1), 132.1 (8 C4), 121.1 (4 C), −1.1 (36 C). 29Si[1H] NMR (CDCl3): δ = −14.3 (4 Si), −3.9 (12 Si). Anal. calc'd for C152H180N4Si16Zn·EtOH (2619.02): C, 70.49; H, 7.14; N, 2.14. Found: C, 70.51; H, 6.95; N, 1.86.
121.1 (4 C), 114.0 (24 C), 21.6 (24 C), −5.8 (12 C). 29Si (1H) NMR (CDCl3): δ = −14.2 (4 Si), −5.7 (12 Si). Anal. calcld for C_{20}H_{28}N_{4}Si_{16}Zn-2EtOH (3294.87): C, 74.36; H, 7.34; N, 1.70. Found: C, 74.21; H, 7.30; N, 1.78.

X-ray crystallography

Single crystal X-ray diffraction measurements of 3b,c, 4a and 9b were performed with a Bruker Smart 1k CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å), while for data collection of 6a an Oxford Gemini S diffractometer and Cu Kα radiation (λ = 1.54184 Å) was used. Table S1† summarizes selected crystal and structural refinement data of 3b,c, 4a, 6a and 9b. All structures were solved by direct methods using the SHELXLS-97 and refined by full-matrix least-squares procedures on F2 using the SHELXL-97 as part of the software package SHELXL. 66 All non-hydrogen atoms were refined anisotropically. All C-, N- and O-bonded hydrogen atoms were refined using a riding model. Only in the case of 3c the positions of N-bonded hydrogen atoms could be taken from the difference Fourier map and were refined freely. For 3b the atoms C52–C54 have been refined disordered on three positions with occupation factors of 0.26, 0.20 and 0.54. Furthermore, the CH2 group of the partially occupied CH2Cl2 (occupation factor 1/4) packing solvent molecule has been refined to split occupancies of 0.94 and 0.06. In the case of 3c the atoms C23–C29 and C30–C36 have been refined disordered with split occupancies of 0.68/0.32 and 0.51/0.49, respectively. In the case of 4a the atoms C38–C42 and C49–C53 have been refined disordered with split occupancies of 0.36/0.64 and 0.72/0.28, respectively. For 6a one thf packing solvent molecule (O6, C70–C73) has been refined disordered with split occupancies of 0.47 and 0.53. Furthermore, atoms O1, O2 and O3 are disordered and have been refined to split occupancies of 0.54/0.46, 0.50/0.50 and 0.50/0.50, respectively. In the case of 9b the atoms C25/C26, C36/C37 and C126 have been disordered with split occupancies of 0.76/0.24, 0.57/0.43 and 0.52/0.48, respectively. Furthermore, the ethyl group (C110, C12O) of one partially occupied EtOH molecule (occupation factor 1/2) has been refined to split occupancies of 0.32 and 0.68.

Data have been deposited at the Cambridge Crystallographic Data Centre under the CCDC deposition numbers 976300 (3c), 976301 (3b), 976302 (4a), 976303 (6a) and 976304 (9a).

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39 It needs to be emphasized that for 3b, 3c, 4a and 9b, π–π interactions involving the terminal allylic side chains have been left unattended. The allyl groups have been at least partially refined disordered, if possible. Moreover, the respective carbon atoms do have comparatively large U_eq values. Due to that it appears less trustworthy to assign for them π–π interactions correctly apart from attractive van der Waals forces.
(a) Labelling code: symmetry generated equivalent atoms of Si10, Si11–Si16/C101, C102–C188 are assigned as Si0#, Si1#–Si6#/C1# and C2#–C88#. Of symmetry generated carbon atoms only selected ones have been labelled. Atom C126 is disordered on two positions of which only one is displayed and labelled with C12A (b) The assignment of symmetry generated atoms is for 9b more complicated than in conventional cases, as four digits are allowed only when working with crystallographic software. For example, for 9bB the atomic labelling of atom Si16 is trivial, its symmetry generated equivalent by applying the crystallographically imposed inversion symmetry should be then labelled as Si16A. A second full molecule of 9bB, fully symmetry generated, should then have the atom labelling Si16B and Si16BA. Such a labelling code is not accessible. Therefore, the following restrictions were applied:

9bA: Atoms generated by crystallographically imposed molecular inversion symmetry are labelled with the suffix “A”.

9bA: (2nd full molecule)
1st half: N1, N2, Si1–Si8 and C1–C83 labelled with the suffix “B”
2nd half: N1A and N2A labelled as N1AB and N2AB
C1A–C9A labelled as C1B–C9B
Si1A–Si8A and C10A–C83A labelled as Si1’–Si8’ and C10’–C83’

9bB: Atoms generated by crystallographically imposed molecular inversion symmetry labelled as follows
N3, N4 and Si9 labelled with the suffix “A”
Si10–Si16 and C101–C183 labelled as Si0#–Si6# and C1#–C83#

9bB: (2nd full molecule)
1st half: N3, N4 and Si9 labelled with suffix “B”
C101–C109 labelled as C01B–C09B
Si10–Si16 and C110–C183 labelled as Si0+–Si6+ and C10+–C83+
2nd half: N3A and N4A labelled as N3AB, N4AB
Si9A–Si16A and C101A–C183A labelled as Si9’–Si6’ and C101’–C83’

Note: In the case of labels given in Fig. 14 the suffix “-” has been changed to “$”

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