

Porphyrins with a carbosilane dendrimer periphery
as synthetic components for supramolecular self-
assembly†Zakariyya Ishtaiwi,^a Tobias Rüffer,^a Sami Klaib,^b Roy Buschbeck,^a Bernhard Walfort^a
and Heinrich Lang^{*a}Cite this: *Dalton Trans.*, 2014, **43**,
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The preparation of the shape-persistent carbosilane-functionalized porphyrins $H_2TPP(4-SiRR'Me)_4$, $Zn(II)-TPP(4-SiRR'Me)_4$ ($R = R' = Me$, $CH_2CH=CH_2$, $CH_2CH_2CH_2OH$; $R = Me$, $R' = CH_2CH=CH_2$, $CH_2CH_2CH_2OH$; $TPP =$ tetraphenyl porphyrin), $H_2TPP(4-Si(C_6H_4-1,4-SiRR'Me)_3)_4$, and $Zn(II)-TPP(4-Si(C_6H_4-1,4-SiRR'Me)_3)_4$ ($R = R' = Me$, $CH_2CH=CH_2$; $R = Me$, $R' = CH_2CH=CH_2$) 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 $\pi-\pi$ 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.

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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 spherical arrangement with 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),^{8b,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.^{11a,14b,15} 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

^aTechnische Universität Chemnitz, Faculty of Natural Sciences,
Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany.
E-mail: heinrich.lang@chemie.tu-chemnitz.de; Fax: +49-(0)371-531-21219;
Tel: +49-(0)371-531-21210

^bTafila Technical University, Faculty of Science, Department of Chemistry and
Chemical Technology, Tafila, Jordan

†Electronic supplementary information (ESI) available: X-ray crystal structure data. Fig. S1/S2 and Fig. S3 display the crystal structure of **3c** and **6a**, respectively, with respect to the orientation of the unit cell. Table S1 gives crystal and intensity collection data of **3b-1/4CH₂Cl₂**, **3c**, **4a**, **6a-2thf** and **9b-3.5EtOH**. Fig. S4–S6 illustrate T-shaped $\pi-\pi$ interactions in the crystal structure of **9b-3.5EtOH**. Table S2 gives selected geometric features of intermolecular hydrogen bonds of **6a**. Table S3 gives structural parameters of the porphyrin cores of **3b**, **3c**, **4a**, **6a** and **9b**. Fig. S7 illustrates geometrical features of saddling distorted porphyrins. Fig. S8 shows the atom labelling for the NMR data. CCDC 976300–976304. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53535e

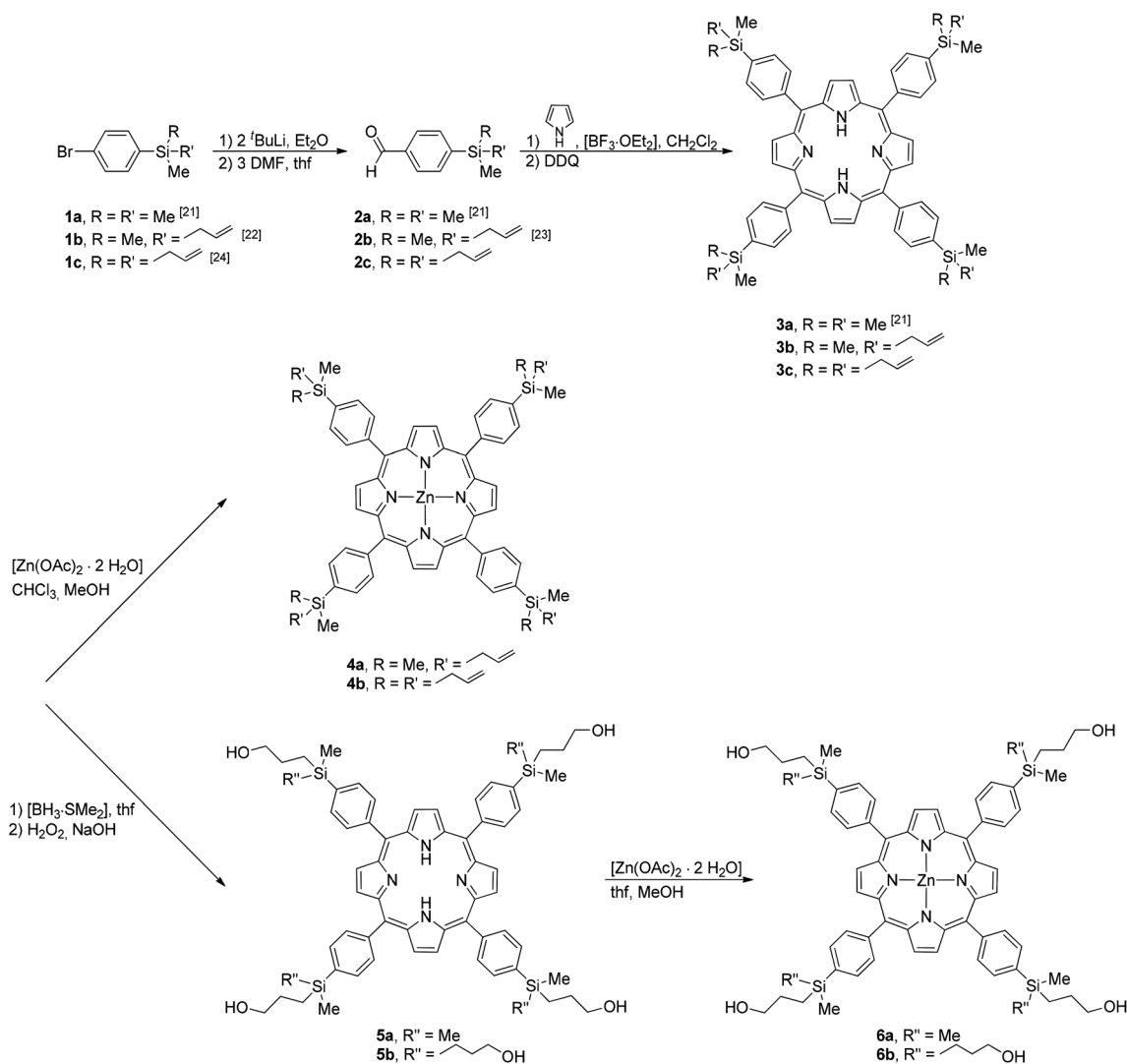
Recently, we got interested in the synthesis of $\text{SiCH}_2\text{CH}=\text{CH}_2$ - and $\text{Si}(\text{CH}_2)_3\text{OH}$ -functionalized tetraphenyl porphyrins and to use them as supramolecular tectons in the formation of ordered network arrays, since this family of compounds provides a relatively 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.²⁰ In this respect, the carbosilane aldehydes $\text{H}(\text{O})\text{C}-1-\text{C}_6\text{H}_4-4-\text{SiRR}'\text{Me}$ (**2a**, $\text{R} = \text{R}' = \text{Me}$; **2b**, $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; **2c**, $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$), accessible by the consecutive treatment of 1-Br- $\text{C}_6\text{H}_4-4-\text{SiRR}'\text{Me}$ (**1a**, $\text{R} = \text{R}' = \text{Me}$; **1b**, $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; **1c**, $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$) with $t\text{BuLi}$ and dimethylformamide, were reacted with pyrrole in the presence of catalytic amounts of $[\text{BF}_3 \cdot \text{OEt}_2]$ followed by addition of 2,3-dichloro-5,6-dicyanobenzoquinone (= DDQ) in CH_2Cl_2 solutions at ambient temperature (Scheme 1, Experimental section). The appropriate porphyrins $\text{H}_2\text{TPP}(4-\text{SiRR}'\text{Me})_4$ (**3a**, $\text{R} = \text{R}' = \text{Me}$; **3b**, $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; **3c**, $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; 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 $\text{Zn-TPP}(4-\text{SiRR}'\text{Me})_4$ (**4a**, $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; **4b**, $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$) were obtained in virtually quantitative yields upon treatment of **3b** or **3c** with zinc(II) acetate in a mixture of CHCl_3 -MeOH (ratio 5 : 1, v/v) (Scheme 1, see the Experimental section).



Scheme 1 Synthesis of 2–6.^{21–24}

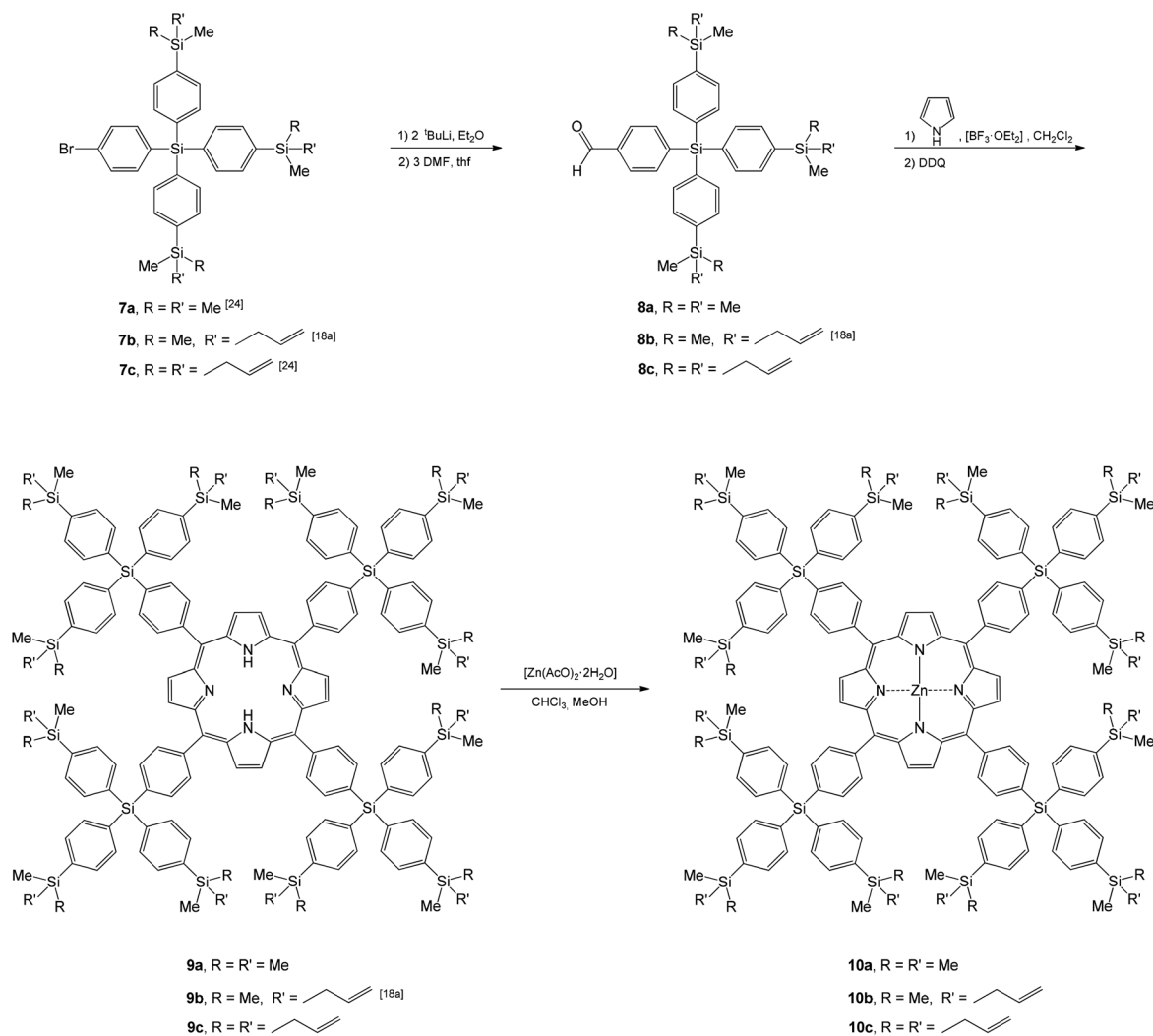


Porphyrins **3b** and **3c**, respectively, with their terminal $\text{SiCH}_2\text{CH}=\text{CH}_2$ units could successfully be converted to the corresponding Si-propanolic-functionalized porphyrins **5a** and **5b** by a consecutive hydroboration–oxidation procedure (Scheme 1, see the Experimental section). Hydroboration of the appropriate end-grafted allyl groups with $[\text{BH}_3\cdot\text{dms}]$ (dms = dimethyl sulfoxide) in thf gave the corresponding BH_2 -functionalized systems, which on addition of hydrogen peroxide were oxidized to the respective alcohols $\text{H}_2\text{TPP-(4-SiRR''Me)}_4$ (**5a**, $\text{R} = \text{Me}$, $\text{R''} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; **5b**, $\text{R} = \text{R''} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) (Scheme 1). These porphyrins produce, when reacted with the transition metal salt $[\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}]$, the expected zinc(II) species $\text{Zn(II)-TPP(4-SiRR''Me)}_4$ (**6a**, $\text{R} = \text{Me}$, $\text{R''} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; **6b**, $\text{R} = \text{R''} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) in virtually quantitative yield (Scheme 1, see the Experimental section). Zinc porphyrins **6a** and **6b** dissolve in most common organic solvents.

The synthesis procedure used in the preparation of **3–6** (Scheme 1) could successfully be transferred to the synthesis of the 1st generation carbosilane-based porphyrins **9a–c** and **10a–c**

(Scheme 2). The therefore necessary key aldehyde starting materials $1\text{-H(O)C-C}_6\text{H}_4\text{-4-Si(C}_6\text{H}_4\text{-1,4-SiRR'Me)}_3$ (**8a**, $\text{R} = \text{R}' = \text{Me}$; **8b**, $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; **8c**, $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$) were obtained with a two-step synthesis procedure from $1\text{-Br-C}_6\text{H}_4\text{-4-Si(C}_6\text{H}_4\text{-1,4-SiRR'Me)}_3$ (**7a**, $\text{R} = \text{R}' = \text{CH}_3$; **7b**, $\text{R} = \text{CH}_3$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$; **7c**, $\text{R} = \text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$).

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)-porphyrins **4**, **6** and **10** was quantitative (see the Experimental section). All carbosilane-functionalized (metallo)porphyrins 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 porphyrins **3–6** and **9–10** were characterized by elemental analysis, IR, UV-Vis and NMR spectroscopy (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$) (see the Experimental section). ESI-TOF mass spectrometric measurements were additionally carried out with selected metal-free and zinc(II) metallated samples



Scheme 2 Synthesis of **8–10**.^{18a,24}



(**2c**, **3b,c**, **4a,b**, **5a,b**, **6a,b** and **8a,c**). The identity of **3b,c**, **4a**, **6a** and **9b** in the solid state was confirmed by single X-ray diffraction studies (*vide infra*).

The IR spectra of the newly synthesized allyl carbosilane-based porphyrins (Schemes 1 and 2) show a characteristic $\nu_{C=C}$ 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 CH_3 bending vibration of the SiMe_n entities ($n = 1, 2, 3$) is observed at *ca.* 1250 cm^{-1} . These findings are in agreement with allyl-functionalized carbosilanes, *i.e.* $\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ (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 $[\text{BH}_3\text{-SMe}_2]$, since the $\nu_{C=C}$ vibration of the allylic units in the respective starting compounds (*ca.* 1630 cm^{-1}) disappears in the course of the reaction. After H_2O_2 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.²⁶ Solely broad absorptions are observed in the IR spectra; hydrogen-bridge formation and hence formation of molecular networks are the most obvious.²⁷

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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.²⁸ 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 SiMe , $\text{Si}(\text{CH}_2)_3\text{Me}$, and $\text{SiCH}_2\text{CH}=\text{CH}_2$ 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 $\text{Si}(\text{CH}_2)_3\text{OH}$ building blocks are found (see the Experimental section). Similar to the IR spectra, the representative resonance signals for the $\text{SiCH}_2\text{CH}=\text{CH}_2$ groups in **3b** and **3c** at *ca.* 2.0 (SiCH_2), 5.0 ($\text{H}_2\text{C}=\text{}$) and 6.0 ppm ($\text{CH}=\text{}$) (in CDCl_3) disappear on hydroboration and after oxidation with H_2O_2 new signals can be found at 0.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 1.7 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.5 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$) and 4.5 ppm ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$) for alcohols **5a** and **5b** (in $\text{dmsO}-d_6$), respectively. Similar observations were made in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic studies (see the Experimental section).

Additionally, the $^{29}\text{Si}\{^1\text{H}\}$ 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 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **9** and **10** (in CDCl_3) show, as expected, two resonance signals at *ca.* –14.5 ppm and between –3.9 and –5.7 ppm, which can be assigned to the core and terminal silicon atoms (see the Experimental section).²⁴ The values for the inner silicon atoms are in good agreement with tetraphenyl silane (–14.98 ppm).²⁹

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 $[\text{M} + \text{H}]^+$, while for **4a,b** $[\text{M}]^+$ is characteristic. Compounds **5b**, **6a,b** and **8a,c** could successfully be ionized by doping with KSCN and hence the ion $[\text{M} + \text{K}]^+$ 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 CH_2Cl_2 and thf as solvents (Table 1). The porphyrin core of **3b** shows one Soret band at 420 nm in CH_2Cl_2 and four Q bands at 517, 552, 592 and 648 nm (Fig. 1a).³⁰ Metallation of **3b** with zinc(II) did not influence the position of the Soret band (**4a**, 421 nm, in CH_2Cl_2) (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 CH_2Cl_2 , which is typical for metallo-porphyrins.³¹ 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 scaffold^{30b,c} 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.³²

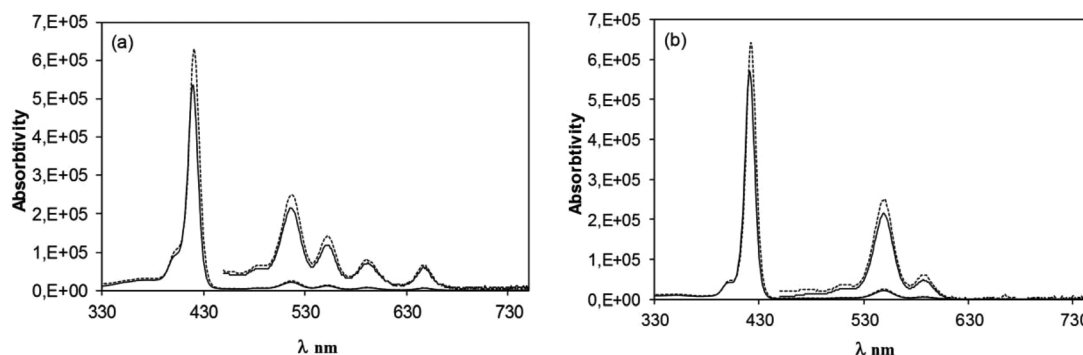
X-ray investigations

Single crystals of **3b** (as **3b-1/4CH₂Cl₂**), **3c**, **4a** and **9b** (as **9b-3.5EtOH**) were grown by slow diffusion of CH_2Cl_2 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 *n*-pentane at ambient temperature. The molecular structures of **3b,c**, **4a** and **6a** are displayed in Fig. 2,



Table 1 UV-Vis absorptions of porphyrins 3–6, 9 and 10

Compound (solvent)	λ_{\max} (nm) (log ϵ)	Soret band (nm) (log ϵ)	Q bands (nm) (log ϵ)			
3b (CH ₂ Cl ₂)		420 (5.73)	517 (4.35)	552 (4.09)	592 (3.87)	648 (3.77)
3b (thf)		419 (5.68)	515 (4.28)	550 (4.01)	593 (3.73)	648 (3.67)
3c (CH ₂ Cl ₂)		420 (5.78)	517 (4.39)	552 (4.14)	592 (3.92)	648 (3.85)
3c (thf)		419 (5.72)	515 (4.32)	550 (4.05)	593 (3.77)	649 (3.70)
4a (CH ₂ Cl ₂)	402 (4.61)	421 (5.75)		549 (4.33)	588 (3.67)	
4a (thf)	405 (4.68)	425 (5.83)		558 (4.36)	598 (3.98)	
4b (CH ₂ Cl ₂)	402 (4.71)	421 (5.83)		549 (4.42)	588 (3.76)	
4b (thf)	405 (4.67)	426 (5.83)		558 (4.36)	597 (3.97)	
9a (CH ₂ Cl ₂)		421 (5.76)	517 (4.38)	552 (4.14)	592 (3.91)	648 (3.84)
9a (thf)		420 (5.76)	515 (4.32)	550 (4.09)	592 (3.80)	648 (3.75)
9b (CH ₂ Cl ₂)		421 (5.80)	517 (4.40)	552 (4.16)	592 (3.91)	648 (3.83)
9b (thf)		420 (5.74)	515 (4.34)	550 (4.10)	592 (3.82)	648 (3.76)
9c (CH ₂ Cl ₂)		421 (5.73)	517 (4.34)	552 (4.09)	592 (3.85)	648 (3.75)
9c (thf)		420 (5.72)	516 (4.32)	550 (4.10)	592 (3.81)	649 (3.75)
10a (CH ₂ Cl ₂)	403 (4.79)	422 (5.92)		550 (4.52)	588 (3.92)	
10a (thf)	406 (4.69)	427 (5.82)		558 (4.38)	598 (4.06)	
10b (CH ₂ Cl ₂)	403 (4.67)	422 (5.81)		550 (4.39)	588 (3.78)	
10b (thf)	406 (4.70)	427 (5.82)		559 (4.39)	598 (4.07)	
10c (CH ₂ Cl ₂)	403 (4.70)	422 (5.82)		550 (4.44)	588 (3.87)	
10c (thf)	407 (4.72)	427 (5.85)		559 (4.40)	598 (4.08)	
5a (CH ₂ Cl ₂)		420 (5.66)	516 (4.24)	552 (3.97)	594 (3.69)	648 (3.69)
5a (thf)		419 (5.68)	516 (4.28)	550 (4.02)	593 (3.73)	650 (3.71)
5b (CH ₂ Cl ₂)		420 (5.66)	517 (4.28)	552 (4.05)	594 (3.81)	648 (3.78)
5b (thf)		419 (5.62)	517 (4.25)	550 (4.03)	594 (3.71)	650 (6.77)
6a (CH ₂ Cl ₂)	403 (4.72)	421 (5.84)		550 (4.24)	588 (3.81)	
6a (thf)	405 (4.59)	426 (5.69)		558 (4.24)	598 (3.91)	
6b (thf)		426 (5.75)		558 (4.31)	598 (4.00)	

Fig. 1 Absorption spectra of **3b** (–) vs. **9b** (···) (a) and **4a** (–) vs. **10b** (···) (b) in CH₂Cl₂.

6, 3 and 8. 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.

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 *C*₁ 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]porphyrin^{32a} 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



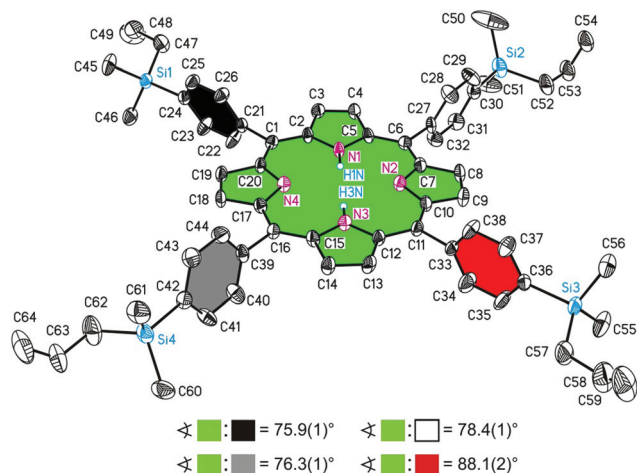


Fig. 2 ORTEP diagram (50% ellipsoid probability) of the molecular structure of **3b**. All C-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign \angle refers to calculated interplanar angles between terminal C_6H_4 groups and the central $\text{C}_{20}\text{N}_4\text{H}_2$ core.

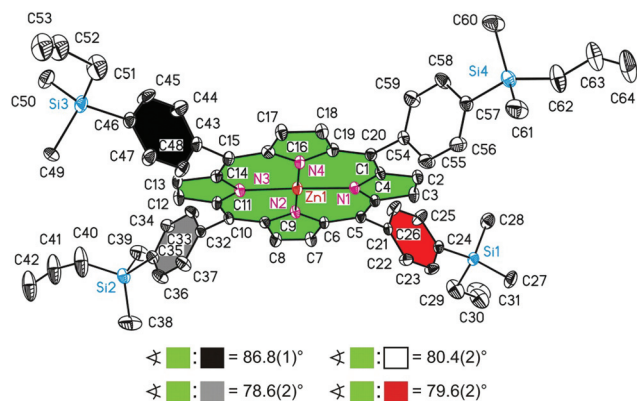


Fig. 3 ORTEP diagram (50% ellipsoid probability) of the molecular structure of **4a**. All hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign \angle refers to calculated interplanar angles between terminal C_6H_4 groups and the central $\text{C}_{20}\text{N}_4\text{Zn}$ core.

Fig. 2 and 3. Both porphyrins crystallize in the tetragonal space group $P4_3$ with similar dimensions of their respective unit cells (Table S1†). For **3b** a partially occupied packing solvent molecule of CH_2Cl_2 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 C_{20}N_4 cores of **3b** and **4a** can be considered as identical to each other within standard deviations (Tables 2 and 3). Not surprisingly, the $\text{N}\cdots\text{N}$ distances of opposite nitrogen atoms of **3b** are significantly longer, when compared with **4a** (**3b**, $\text{N}1\cdots\text{N}3/\text{N}2\cdots\text{N}4 = 4.160(5)/4.113(5)$ Å

Table 2 Selected bond lengths (Å) of **3b**, **1/4** CH_2Cl_2 , **3c**, **4a**, **6a**, **2thf** and **9b**, **3.5EtOH**

3b-1/4CH ₂ Cl ₂	3c	4a	6a-2thf	9b-3.5EtOH
C1–C2	1.399(6)	C11–C12	C11–C12	C12–C13
C2–C3	1.448(5)	C12–C13	C11–C12	C13–C14
C3–C4	1.361(5)	C13–C14	C12–C13	C14–C15
C4–C5	1.365(4)	C14–C15	C13–C14	C15–C16
C5–C6	1.368(4)	N3–C12	C13–C14	C16–C17
C6–C7	1.376(4)	N3–C15	C13–C14	C17–C18
C7–C8	1.395(5)	C15–C16	C14–C15	C18–C19
C8–C9	1.413(6)	C16–C17	C15–C16	C19–C20
C9–C10	1.448(5)	C17–C18	C16–C17	C20–C21
C10–C11	1.357(6)	C18–C19	C17–C18	C21–C22
C11–C12	1.454(5)	C19–C20	C18–C19	C22–C23
C12–C13	1.350(5)	C20–C21	C19–C20	C23–C24
C13–C14	1.457(5)	C21–C22	C20–C21	C24–C25
C14–C15	1.390(5)	C22–C23	C21–C22	C25–C26
C15–C16	1.371(4)	C23–C24	C22–C23	C26–C27
C16–C17	1.385(5)	C24–C25	C23–C24	C27–C28
C17–C18	1.427(5)	C25–C26	C24–C25	C28–C29
C18–C19	1.350(5)	C26–C27	C25–C26	C29–C30
C19–C20	1.457(5)	C27–C28	C26–C27	C30–C31
C20–C21	1.385(5)	C28–C29	C27–C28	C31–C32
C21–C22	1.371(4)	C29–C30	C28–C29	C32–C33
C22–C23	1.427(5)	C30–C31	C29–C30	C33–C34
C23–C24	1.502(5)	C31–C32	C30–C31	C34–C35
C24–C25	1.520(5)	C32–C33	C31–C32	C35–C36
C25–C26	4.160(5)	C33–C34	C32–C33	C36–C37
C26–C27		C34–C35	C33–C34	C37–C38
C27–C28		C35–C36	C34–C35	C38–C39
C28–C29		C36–C37	C35–C36	C39–C40
C29–C30		C37–C38	C36–C37	C40–C41
C30–C31		C38–C39	C37–C38	C41–C42
C31–C32		C39–C40	C38–C39	C42–C43
C32–C33		C40–C41	C39–C40	C43–C44
C33–C34		C41–C42	C40–C41	C44–C45
C34–C35		C42–C43	C41–C42	C45–C46
C35–C36		C43–C44	C42–C43	C46–C47
C36–C37		C44–C45	C43–C44	C47–C48
C37–C38		C45–C46	C44–C45	C48–C49
C38–C39		C46–C47	C45–C46	C49–C50
C39–C40		C47–C48	C46–C47	C50–C51
C40–C41		C48–C49	C47–C48	C51–C52
C41–C42		C49–C50	C48–C49	C52–C53
C42–C43		C50–C51	C49–C50	C53–C54
C43–C44		C51–C52	C50–C51	C54–C55
C44–C45		C52–C53	C51–C52	C55–C56
C45–C46		C53–C54	C52–C53	C56–C57
C46–C47		C54–C55	C53–C54	C57–C58
C47–C48		C55–C56	C54–C55	C58–C59
C48–C49		C56–C57	C55–C56	C59–C60
C49–C50		C57–C58	C56–C57	C60–C61
C50–C51		C58–C59	C57–C58	C61–C62
C51–C52		C59–C60	C58–C59	C62–C63
C52–C53		C60–C61	C59–C60	C63–C64
C53–C54		C61–C62	C60–C61	C64–C65
C54–C55		C62–C63	C61–C62	C65–C66
C55–C56		C63–C64	C62–C63	C66–C67
C56–C57		C64–C65	C63–C64	C67–C68
C57–C58		C65–C66	C64–C65	C68–C69
C58–C59		C66–C67	C65–C66	C69–C70
C59–C60		C67–C68	C66–C67	C70–C71
C60–C61		C68–C69	C67–C68	C71–C72
C61–C62		C69–C70	C68–C69	C72–C73
C62–C63		C70–C71	C69–C70	C73–C74
C63–C64		C71–C72	C70–C71	C74–C75
C64–C65		C72–C73	C71–C72	C75–C76
C65–C66		C73–C74	C72–C73	C76–C77
C66–C67		C74–C75	C73–C74	C77–C78
C67–C68		C75–C76	C74–C75	C78–C79
C68–C69		C76–C77	C75–C76	C79–C80
C69–C70		C77–C78	C76–C77	C80–C81
C70–C71		C78–C79	C77–C78	C81–C82
C71–C72		C79–C80	C78–C79	C82–C83
C72–C73		C80–C81	C79–C80	C83–C84
C73–C74		C81–C82	C80–C81	C84–C85
C74–C75		C82–C83	C81–C82	C85–C86
C75–C76		C83–C84	C82–C83	C86–C87
C76–C77		C84–C85	C83–C84	C87–C88
C77–C78		C85–C86	C84–C85	C88–C89
C78–C79		C86–C87	C85–C86	C89–C90
C79–C80		C87–C88	C86–C87	C90–C91
C80–C81		C88–C89	C87–C88	C91–C92
C81–C82		C89–C90	C88–C89	C92–C93
C82–C83		C90–C91	C89–C90	C93–C94
C83–C84		C91–C92	C90–C91	C94–C95
C84–C85		C92–C93	C91–C92	C95–C96
C85–C86		C93–C94	C92–C93	C96–C97
C86–C87		C94–C95	C93–C94	C97–C98
C87–C88		C95–C96	C94–C95	C98–C99
C88–C89		C96–C97	C95–C96	C99–C100
C89–C90		C97–C98	C96–C97	C100–C101
C90–C91		C98–C99	C97–C98	C101–C102
C91–C92		C99–C100	C98–C99	C102–C103
C92–C93		C100–C101	C99–C100	C103–C104
C93–C94		C101–C102	C100–C101	C104–C105
C94–C95		C102–C103	C101–C102	C105–C106
C95–C96		C103–C104	C102–C103	C106–C107
C96–C97		C104–C105	C103–C104	C107–C108
C97–C98		C105–C106	C104–C105	C108–C109
C98–C99		C106–C107	C105–C106	C109–C110
C99–C100		C107–C108	C106–C107	C110–C111
C100–C101		C108–C109	C107–C108	C111–C112
C101–C102		C109–C110	C108–C109	C112–C113
C102–C103		C110–C111	C109–C110	C113–C114
C103–C104		C111–C112	C110–C111	C114–C115
C104–C105		C112–C113	C111–C112	C115–C116
C105–C106		C113–C114	C112–C113	C116–C117
C106–C107		C114–C115	C113–C114	C117–C118
C107–C108		C115–C116	C114–C115	C118–C119
C108–C109		C116–C117	C115–C116	C119–C120
C109–C110		C117–C118	C116–C117	C120–C121
C110–C111		C118–C119	C117–C118	C121–C122
C111–C112		C119–C120	C118–C119	C122–C123
C112–C113		C120–C121	C119–C120	C123–C124
C113–C114		C121–C122	C120–C121	C124–C125
C114–C115		C122–C123	C121–C122	C125–C126
C115–C116		C123–C124	C122–C123	C126–C127
C116–C117		C124–C125	C123–C124	C127–C128
C117–C118		C125–C126	C124–C125	C128–C129
C118–C119		C126–C127	C125–C126	C129–C130
C119–C120		C127–C128	C126–C127	C130–C131
C120–C121		C128–C129	C127–C128	C131–C132
C121–C122		C129–C130	C128–C129	C132–C133
C122–C123		C130–C131	C129–C130	C133–C134
C123–C124		C131–C132	C130–C131	C134–C135
C124–C125		C132–C133	C131–C132	C135–C136
C125–C126		C133–C134	C132–C133	C136–C137
C126–C127		C134–C135	C133–C134	C137–C138
C127–C128		C135–C136	C134–C135	C138–C139
C128–C129		C136–C137	C135–C136	C139–C140
C129–C130		C137–C138	C136–C137	C140–C141
C130–C131		C138–C139	C137–C138	C141–C142
C131–C132		C139–C140	C138–C139	C142–C143
C132–C133		C140–C141	C139–C140	C143–C144
C133–C134		C141–C142	C140–C141	C144–C145
C134–C135		C142–C143	C141–C142	C145–C146
C135–C136		C143–C144	C142–C143	C146–C147
C136–C137		C144–C145	C143–C144	C147–C148
C137–C138		C145–C146	C144–C145	C148–C149
C138–C139		C146–C147	C145–C146	C149–C150
C139–C140		C147–C148	C146–C147	C150–C151
C140–C141		C148–C149	C147–C148	C151–C152
C141–C142		C149–C150	C148–C149	C152–C153
C142–C143		C150–C151	C149–C150	C153–C154
C143–C144		C151–C152	C150–C151	C154–C155
C144–C145		C152–C153	C151–C152	C155–C156
C145–C146		C153–C154	C152–C153	C156–C157
C146–C147		C154–C155	C153–C154	C157–C158
C147–C148		C155–C156	C154–C155	C158–C159
C148–C149		C156–C157	C155–C156	C159–C160
C149–C150		C157–C158	C156–C157	C160–C161
C150–C151		C158–C159	C157–C158	C161–C162
C151–C152		C159–C160	C158–C159	C162–C163
C152–C153		C160–C161	C159–C160	C163–C164
C153–C154		C161–C162	C160–C161	C164–C165
C154–C155		C162–C163	C161–C162	C165–C166
C155–C156		C163–C164	C162–C163	C166–C167
C156–C157		C164–C165	C163–C164	C167–C168
C157–C158		C165–C166	C164–C165	C168–C169
C158–C159		C166–C167	C165–C166	C169–C170
C159–C160		C167–C168	C166–C167	C170–C171
C160–C161		C168–C169	C167–C168	C171–C172
C161–C162		C169–C170	C168–C169	C172–C173
C162–C163		C170–C171	C169–C170	C173–C174
C163–C164		C171–C172	C170–C171	C174–C175
C164–C165		C172–C173	C171–C172	C175–C176
C165–C166		C173–C174	C172–C173	C176–C177
C166–C167		C174–C175	C173–C174	C177–C178
C167–C168		C175–C176	C174–C175	C178–C179
C168–C169		C176–C177	C175–C176	C179–C180
C169–C170		C177–C178	C176–C177	C180–C181
C170–C171		C178–C179	C177–C178	C181–C182
C171–C172		C179–C180	C178–C179	C182–C183
C172–C173		C180–C181	C179–C180	C183–C184
C173–C174		C181–C182	C180–C181	C184–C185
C174–C175		C182–C183	C181–C182	C185–C186
C175–C176		C183–C184	C182–C183	C186–C187
C176–C177		C184–C185	C183–C184	C187–C188
C177–C178		C185–C186	C184–C185	C188–C189
C178–C179		C186–C187	C185–C186	C189–C190
C179–C180		C187–C188	C186–C187	C190–C191
C180–C181		C188–C189	C187–C188	C191–C192
C181–C182		C189–C190	C188–C189	C192–C193
C182–C183		C190–C191	C189–C190	C193–C194
C183–C184		C191–C192	C190–C191	C194–C195
C184–C185		C192–C193	C191–C192	C195–C196
C185–C186		C193–C194	C192–C193	C196–C197
C186–C187		C194–C195	C193–C194	C197–C198
C187–C188		C195–C196	C194–C195	C198–C199
C188–C189		C196–C197	C195–C196	C199–C200
C189–C190		C197–C198	C196–C197	C200–C201
C190–C191		C198–C199	C197–C198	C201–C202
C191–C192		C199–C200	C198–C199	C202–C203
C192–C193		C200–C201	C199–C200	C203–C204
C193–C194		C201–C202	C200–C201	C204–C205
C194–C195		C202–C203	C201–C202	C205–C206
C195–C196		C203–C204	C202–C203	C206–C207
C196–C197		C204–C205	C203–C204	C207–C208
C197–C198		C205–C206	C204–C205	C208–C209
C198–C199		C206–C207	C205–C206	C209–C210
C199–C200		C207–C208	C206–C207	C210–C211
C200–C201		C208–C209	C207–C208	C211–C212
C201–C202		C209–C210	C208–C209	C212–C213
C202–C203		C210–C211	C209–C210	C213–C214
C203–C204		C211–C212	C210–C211	C214–C215
C204–C205		C212–C213	C211–C212	C215–C216
C205–C206		C213–C214	C212–C213	C216–C217
C206–C207		C214–C215	C213–C214	C217–C218
C207–C208		C215–C216	C214–C215	C218–C219
C208–C209		C216–C217	C215–C216	C219–C220
C209–C210		C217–C218	C216–C217	C220–C221
C210–C211		C218–C219	C217–C218	C221–C222
C211–C212		C219–C220	C218–C219	C222–C223
C212–C213		C220–C221	C219–C220	C223–C224
C213–C214		C221–C222	C220–C221	C224–C225
C214–C215		C222–C223	C221–C222	C225–C226
C215–C216		C223–C224		

Table 3 Selected bond angles (°) of **3b**, **1/4CH₂Cl₂**, **3c**, **4a**, **6a-2thf** and **9b-3.5EtOH**

3b-1/4CH₂Cl₂	3c	4a	6a-2thf^c	9b-3.5EtOH
\sum^b	\sum^b	\sum^b	\sum^b	\sum^b
C2-C1-C20	125.0(4)	126.5(2)	124.0(4)	124.5(4)/124.5(4)
C2-C1-C21	118.7(4)	116.4(2)	118.0(4)	117.8(4)/118.0(4)
C20-C1-C21	116.2(3)	117.1(2)	118.0(4)	117.7(4)/117.5(4)
C5-C6-C7	125.6(4)	123.8(2)	125.6(5)	125.3(4)/125.2(4)
C5-C6-C27	117.0(3)	116.9(2)	116.4(4)	118.0(4)/118.2(4)
C7-C6-C27	117.4(3)	119.2(2)	118.0(4)	116.6(4)/116.5(4)
C10-C11-C12	125.4(4)		124.4(4)	
C10-C11-C33	116.7(3)		117.8(4)	
C12-C11-C33	117.9(3)		117.7(4)	
C15-C16-C17	124.6(4)		125.9(4)	
C15-C16-C39	117.9(3)		116.1(4)	
C17-C16-C39	117.5(3)		117.9(4)	
C4-C5-C6	359.9(6)		360.0(7)	360.0(6)
C4-C5-C11				125.0(4)
C6-C5-C11				119.0(3)
C1-C10-C9 ^c	360.0(6)		360.0(8)	116.0(3)
C1-C10-C17 ^c				125.9(4)
C9-C10-C17				116.6(3)
C9-C10-C11	360.0(6)		360.0(8)	117.4(3)
C9-C10-C32				124.4(4)
C11-C10-C32				117.8(4)
C14-C15-C16				117.7(4)
C14-C15-C43				125.9(4)
C16-C15-C43				116.1(4)
N1-Zn1-N3				117.9(4)
N2-Zn1-N4				164.6(1)
N1-Zn1-N2				167.0(1)
N1-Zn1-N4				88.6(1)
N1-Zn1-N3				89.6(1)
N2-Zn1-N3				89.9(1)
N3-Zn1-N4				88.4(1)
C4-C5-C6				359.9(7)
C4-C5-C10				125.0(4)
C6-C5-C10				119.0(3)
C1-C49-C9 ^d				116.0(3)
C1-C49-C50				125.9(6)
C9-C49-C50 ^d				116.6(4)/116.5(4)

^a Angles including atom O4 are not included. ^b \sum = the sum of angles around 5,10,15,20-annellated atoms. ^c Symmetry code: $-x, -y + 2, -z + 1$. ^d Symmetry code: $-x + 2, -y, -z/-x + 1, -y, -z + 1$.

vs. **4a**, $N1 \cdots N3/N2 \cdots N4 = 4.080(5)/4.059(5)$ Å), which nicely reflects the modification of the central $C_{20}N_4$ core upon complexation. The Zn(II) ion of **4a** can be furthermore considered as being involved in an ideal quadratic planar ZnN_4 coordination environment. Zn–N bond lengths of **4a** cover a very narrow range ($Zn1-N4 = 2.019(3)$ to $Zn1-N2 = 2.041(4)$ Å) and N–Zn–N bond angles are very close to the ideal values of *trans*/*cis*-ligated N donor atoms (*trans*: $N1-Zn1-N3/N2-Zn1-N4 = 177.9(3)/178.6(3)^\circ$; *cis*: $N1-Zn1-N4 = 89.3(2)$ to $N1-Zn1-N2 = 90.4(2)^\circ$). Furthermore, the Zn1 atom is located practically in plane with respect to its N_4 environment as it deviates by just 0.007(4) Å of the calculated mean plane of the atoms N1 to N4 (root-mean-square deviation from planarity (rmsd) = 0.030 Å, highest deviation from planarity (hdp) observed for N4 with 0.031(2) Å).

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 C_6H_4 rings are involved in T-shaped π – π contacts³⁴ with the respective $C_{20}N_4$ 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 $H_2TPP(4-SiMe(CH_2CH=CH_2)_2)$ (**3c**) in the solid state is depicted in Fig. 6. The replacement of one methyl group of the carbosilane $SiMe_2(CH_2CH=CH_2)$ 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 $P\bar{1}$ with crystallographically imposed inversion symmetry. Thus, the asymmetric unit of **3c** comprises just half of the molecule, while the 2nd 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 $C_{20}N_4$ 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** ($N1 \cdots N1A/N2 \cdots N2A = 4.325(5)/4.228(5)$ 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*-axis as depicted in Fig. S1 and S2.† Moreover, only the C_6H_4 aromatic group comprising the atoms C11 to C16 and symmetry generated analogues is involved in T-shaped π – π interactions with the $C_{20}N_4$ core of adjacent molecules.



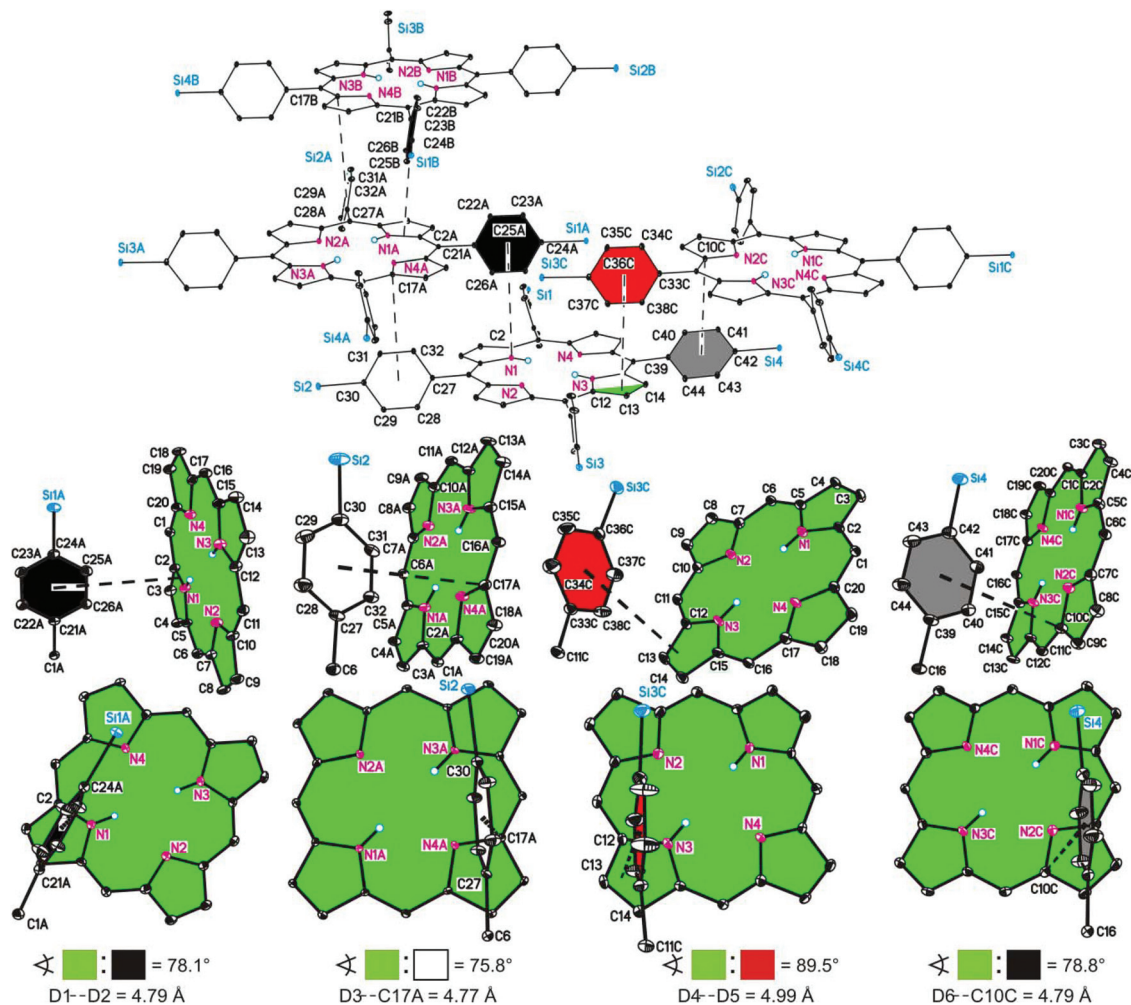


Fig. 4 Above: Graphical illustration of a selected part of the 3D network formed by **3b** due to intermolecular π - π interactions. Labels A-C refer to a 1st-3rd symmetry generated molecule of **3b**. All hydrogen atoms and terminal substituents at the silicon atoms are omitted for clarity. Below: graphical illustration of the four different types of intermolecular π - π interactions between the aromatic C_6H_4 groups with respective parts of the porphyrin core. The sign \angle refers to calculated interplanar angles between differently colored functionalities. Dotted lines indicate the shortest observed distances between the geometrical centroids of the C_6H_4 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.

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 $P\bar{1}$ 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 involved in an approximate square-based pyramidal ZnN₄O coordination environment. Not surprisingly, as a consequence

of the intermolecular O(H)-Zn bond formation the Zn1 atom 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-propyloxy 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

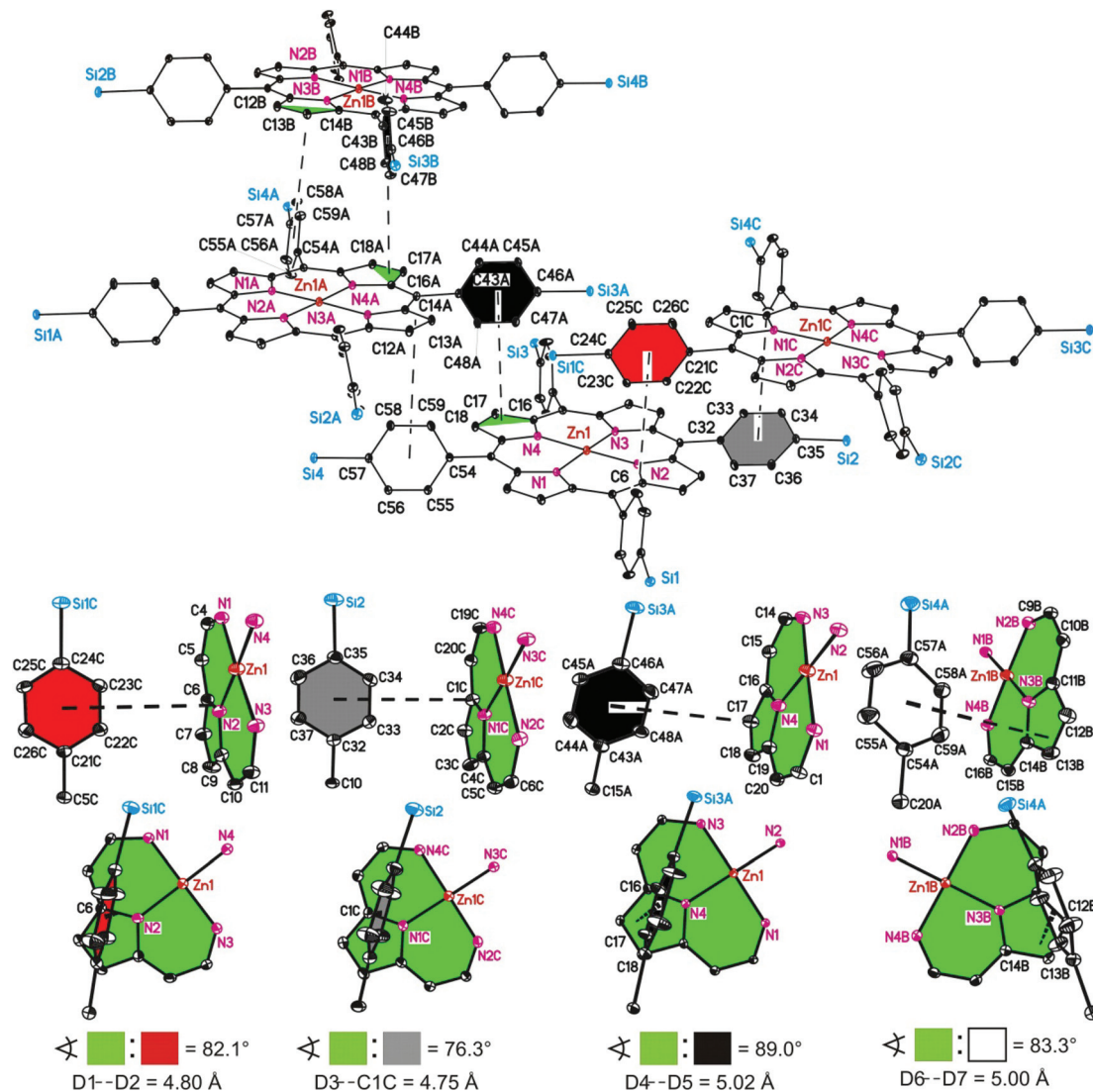


Fig. 5 Above: graphical illustration of a selected part of the 3D network formed by **4a** due to intermolecular π - π interactions. Labels A-C refer to a 1st to the 3rd symmetry generated molecule of **4a**. All hydrogen atoms and terminal substituents at the silicon atoms are omitted for clarity. Below: graphical illustration of the four different types of intermolecular π - π interactions between the aromatic C_6H_4 groups with the respective parts of the porphyrin core. The sign \angle refers to the calculated interplanar angles between differently colored functionalities. Dotted lines indicate the shortest observed distances between the geometrical centroids of the C_6H_4 groups and the respective centroids/atoms of the porphyrin core with D1 = centroid of C21-C26, D3 = centroid of C32-C37, D4 = centroid of C43-C48, D6 = centroid of C54-C59, D2 = centroid of N2 and C6, D5 = centroid of C16-C18, D7 = 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 $H_2TPP(4-Si(C_6H_4-4-Si(CH_2CH=CH_2)Me_2)_3)_4$ (**9b**) crystallises in the triclinic space group $P\bar{1}$. 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 $C_{20}N_4$ 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 C_6H_4 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



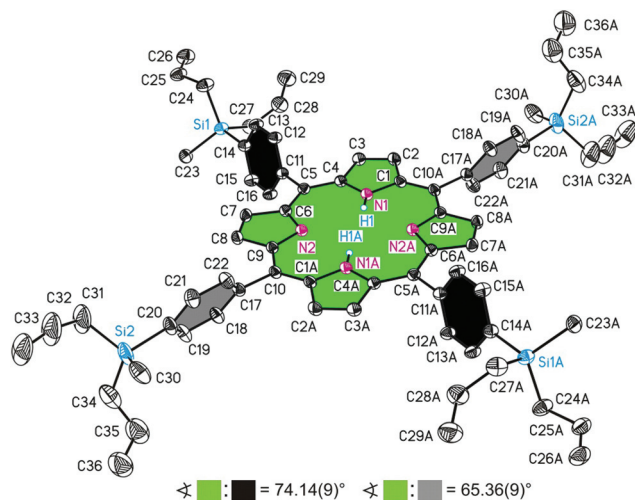


Fig. 6 ORTEP diagram (25% ellipsoid probability) of the molecular structure of **3c**. All C-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign \angle refers to the calculated interplanar angles between terminal C_6H_4 groups and the central $C_{20}N_4H_2$ core. Symmetry code for A: $-x, -y + 2, -z + 1$.

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.⁴¹ In the case of here structurally described porphyrins it can be determined that the central $C_{20}N_4$ 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 $C_{20}N_4$ 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

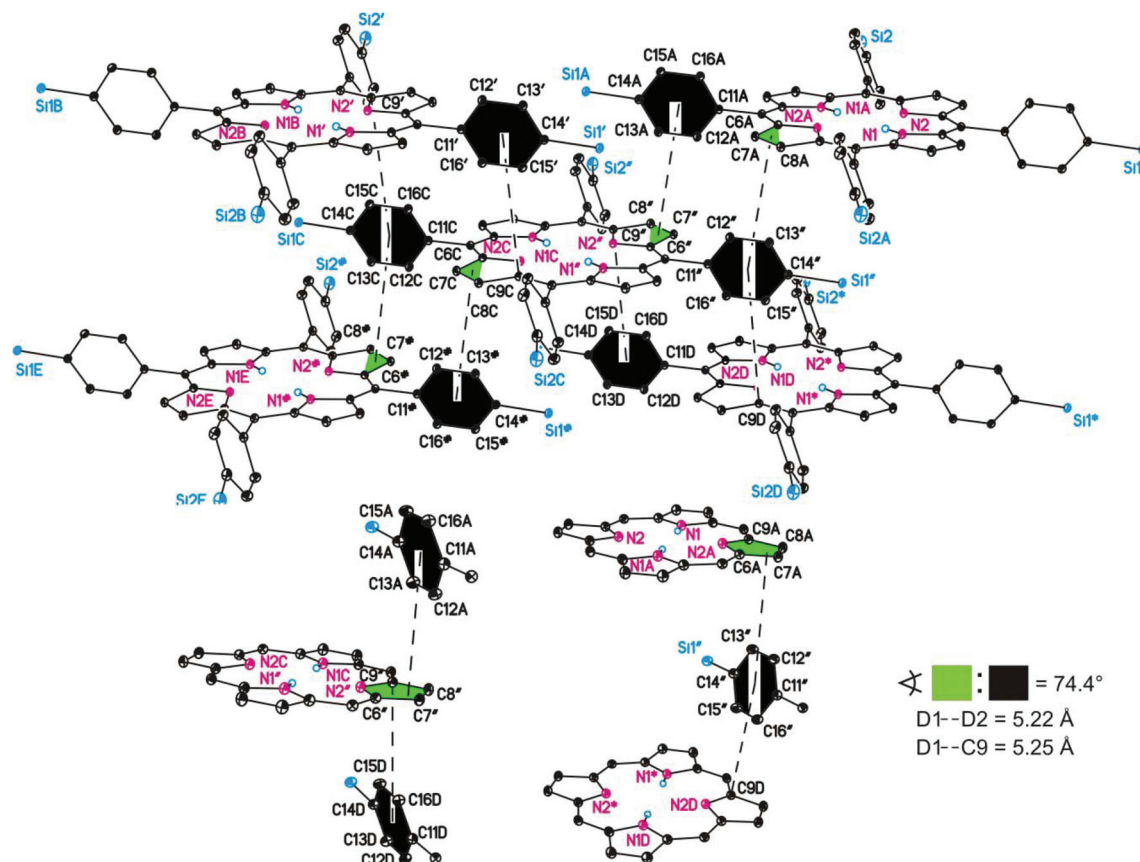


Fig. 7 Above: graphical illustration of a selected part of one 2D layer formed by **3c** due to intermolecular π - π interactions. Labels ', ', * and # refer to symmetry generated atoms of crystallographically independent molecules of the asymmetric unit of **3c**, label A to symmetry generated atoms of the asymmetric unit of **3c** and labels B–E to symmetry generated atoms of A labelled atoms. All C-bonded hydrogen atoms and terminal substituents at the silicon atoms are omitted for clarity. Below: graphical illustration of the intermolecular π - π interactions between the aromatic C_6H_4 groups with the respective parts of the porphyrin core. The sign \angle refers to the calculated interplanar angles between differently coloured functionalities. Dotted lines indicate the shortest observed distances between the geometrical centroids of the C_6H_4 groups and the respective centroids/atoms of the porphyrin core with D1 = centroid of C11–C16 and D2 = centroid of C6–C8, respectively, and symmetry generated related atoms/fragments.



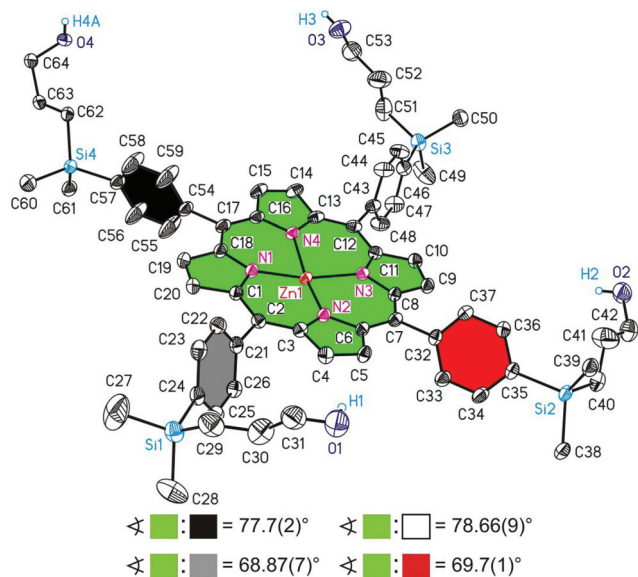


Fig. 8 ORTEP diagram (50% ellipsoid probability) of the molecular structure of **6a**. All C-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign \angle refers to the calculated interplanar angles between terminal C_6H_4 groups and the central $C_{20}N_4Zn$ core.

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-pentamethyldisilanyl)phenylporphyrin^{32a} and 5,10,15,20-tetrakis[4-(diethoxymethylsilyl)phenyl]porphyrin,^{32b} 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.^{32b} 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),⁴² 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.⁴² 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.⁴³ 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

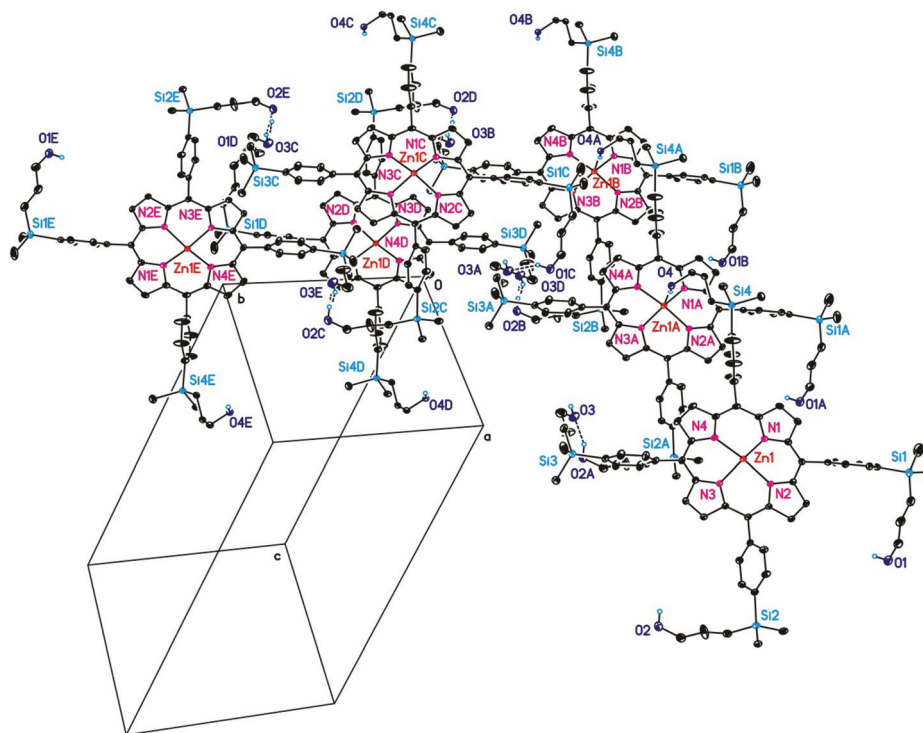


Fig. 9 Graphical representation of a part of one of the 2D layers formed by **6a** in the solid state due to formation of intermolecular O-H...O hydrogen bonds and O(H)-Zn bonds. All C-bonded hydrogen atoms and packing solvent molecules are omitted for clarity. Of disordered atoms only one atomic position is displayed. Labels A-E refer to a 1st-5th symmetry generated molecule of **6a**.



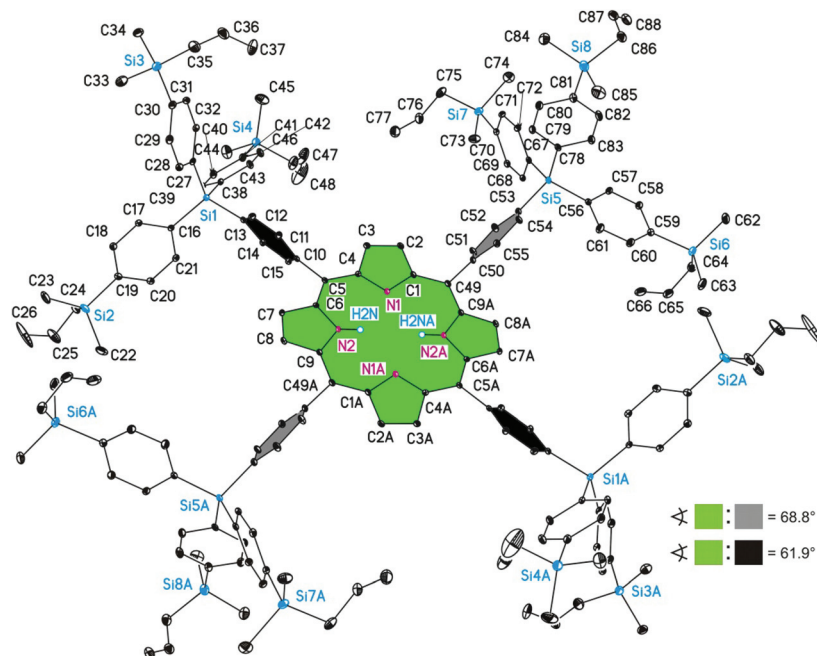


Fig. 10 ORTEP diagram (20% ellipsoid probability) of the molecular structure of **9bA**. All carbon-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign Δ refers to the calculated interplanar angles between the directly porphyrin bonded C_6H_4 groups and the central $C_{20}N_4H_2$ core. Symmetry code for A: $-x + 2, -y, -z$.

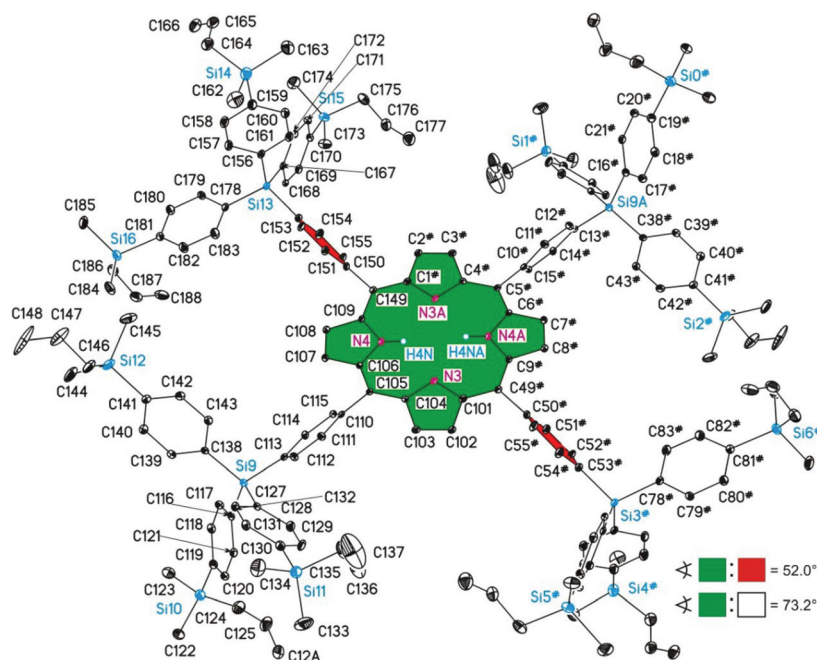


Fig. 11 ORTEP diagram (20% ellipsoid probability) of the molecular structure of **9bB**. All carbon-bonded hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. The sign Δ refers to the calculated interplanar angles between the directly porphyrin bonded C_6H_4 groups and the central $C_{20}N_4H_2$ core. Symmetry code for A: $-x + 1, -y$ and for #: $-z + 1$.^{40a}

Zn(TPP), being co-crystallized with different guest molecules, a review by Byrn *et al.*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 0th and 1st generation carbo-silane dendrimer-based porphyrins of types $H_2TPP(4-SiRR'Me)_4$, $Zn(II)-TPP(4-SiRR'Me)_4$ ($R = R' = Me, CH_2CH=CH_2$,



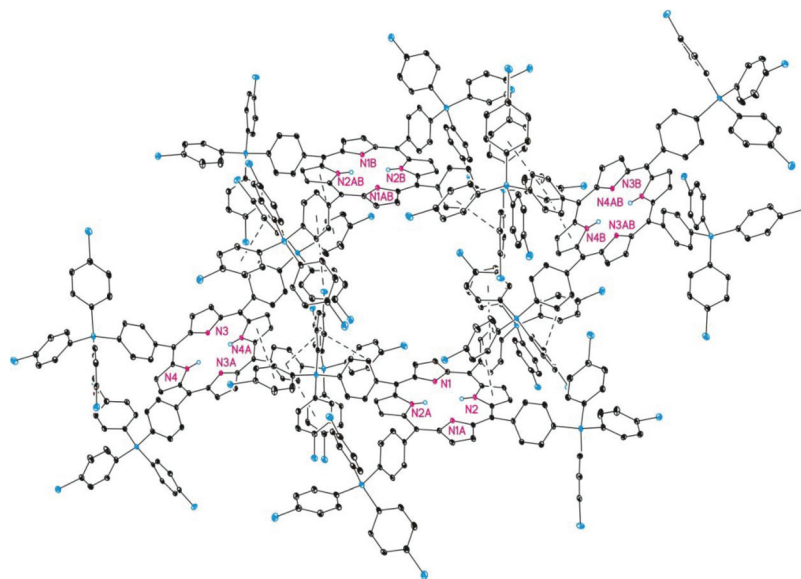


Fig. 12 Selected part of one 2D layer formed by **9b** in the solid state due to T-shaped π - π interactions between molecules of **9bA** and **9bB**.^{40b}

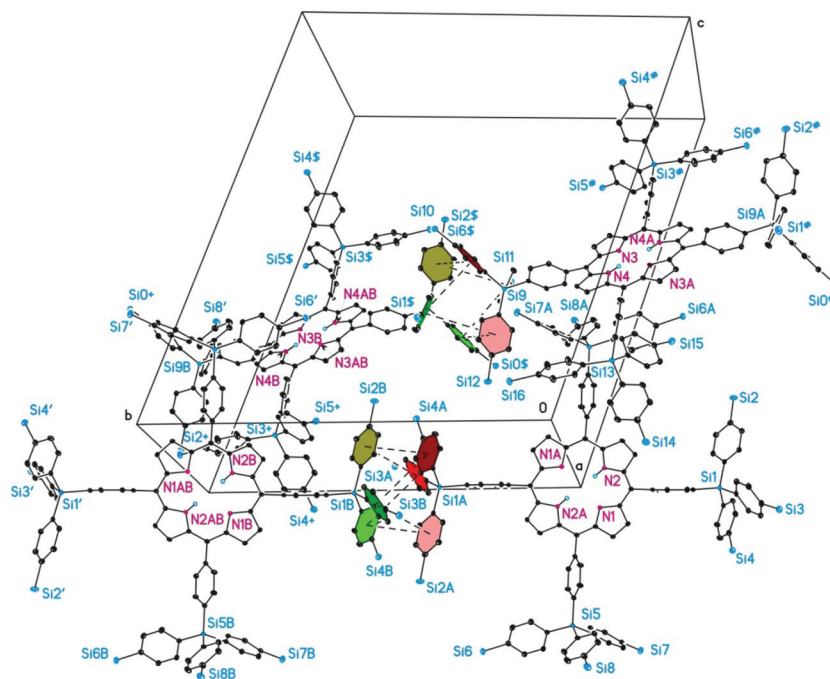


Fig. 13 Graphical illustration of the mutual T-shaped π - π interactions between molecules of **9bA** and **9bB**, being responsible for the connection of the 2D layers of **9b** to give a 3D network structure.^{40b}

$\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; TPP = tetraphenyl porphyrin), $\text{H}_2\text{TPP}(4\text{-Si}(\text{C}_6\text{H}_4\text{-1,4-SiRR}'\text{Me})_3)_4$, and $\text{Zn(II)-TPP}(4\text{-Si}(\text{C}_6\text{H}_4\text{-1,4-SiRR}'\text{Me})_3)_4$ ($\text{R} = \text{R}' = \text{Me}$, $\text{CH}_2\text{CH}=\text{CH}_2$; $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{CH}=\text{CH}_2$) 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.³⁰ 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



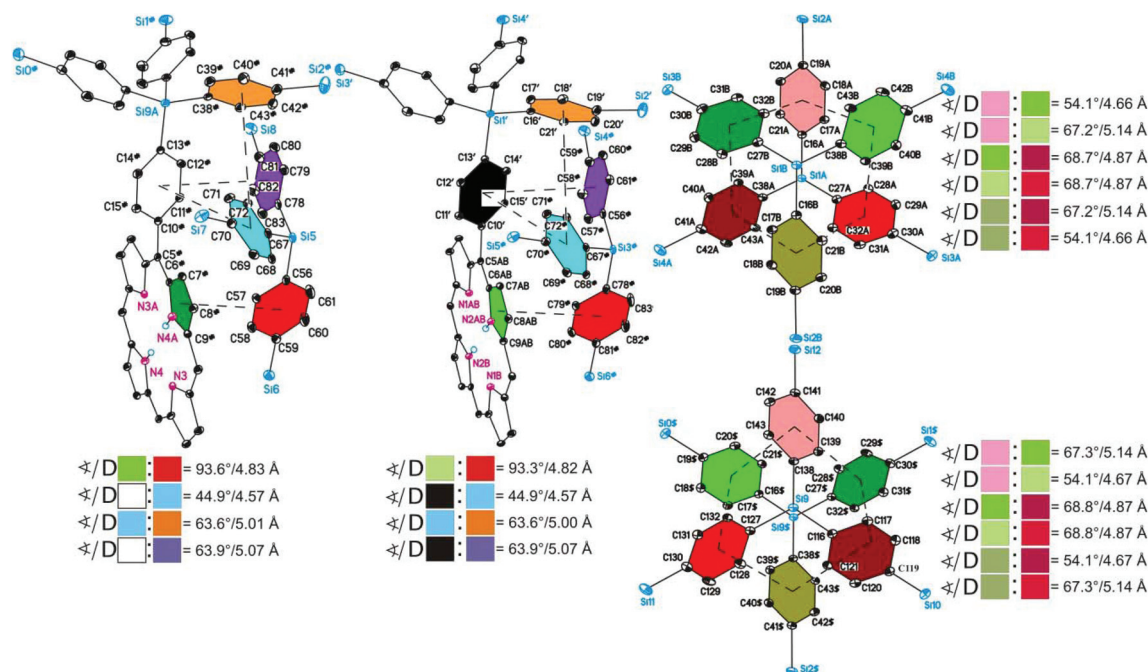


Fig. 14 Graphical illustration of the respective T-shaped π - π interactions observed in the solid state structure of **9b** being responsible for the formation of 2D layers (left and middle) and for the interaction of 2D layers to give a 3D network.^{40b}

can be regarded as isomorphous 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 $C_{20}N_4$ 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 π - π interactions can be observed, although T-shaped π - π 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 π - π 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 n -pentane were purified by distillation from sodium-benzophenone ketyl; CH_2Cl_2 and $CHCl_3$ 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 ($\tilde{\nu}$ 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 (1H NMR at 250.12 MHz and $^{13}C\{^1H\}$ NMR at 62.86 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta = 0.00$ ppm) with the solvent as the reference signal ($CDCl_3$: 1H NMR, $\delta = 7.26$; $^{13}C\{^1H\}$ NMR, $\delta = 77.16$; $DMSO-d_6$: 1H NMR, $\delta = 2.54$; $^{13}C\{^1H\}$ NMR, $\delta = 40.45$; $thf-d_8$: 1H NMR, $\delta = 1.72$; $^{13}C\{^1H\}$ NMR, $\delta = 24.45$).⁴⁵ The atom numbering is depicted in the ESI (Fig. S8†). The assignment of $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ 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- α -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



were purchased from commercial suppliers and were used as received.

4-Diallylmethylsilylbenzaldehyde (2c)

^tBuLi (1.7 M, 34.7 mmol, 20.4 mL, ⁿpentane) 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 thf (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 the organic layer was washed with water (2 × 60 mL), saturated NaHCO₃ (60 mL) and brine (60 mL) and was then dried over MgSO₄. Afterwards, all volatiles were removed in oil-pump vacuum. The crude product was purified by column chromatography (a) ⁿhexane, (b) 20 vol% CH₂Cl₂–ⁿhexane to afford **2c** as colorless oil (14.86 mmol, 3.42 g, 86% based on **1c**).

IR (film): $\tilde{\nu}$ = 3074, 3024, 2992, 2966, 2910, 2882, 2824 (w, CHO), 2732 (w, CHO), 1704 (s, C=O), 1630 (w, C=C), 1254 (w, CH₃ bending), 808 (s, SiC). ¹H NMR (CDCl₃): δ = 10.02 (s, 1 H, CHO), 7.84 (dt, J_{HH} = 8.1 Hz, J_{HH} = 1.6 Hz, 2 H, H³), 7.68 (dt, J_{HH} = 8.1 Hz, 1.6 Hz, 2 H, H⁴), 5.74 (ddt, J_{HH} = 17.6 Hz, J_{HH} = 9.5 Hz, J_{HH} = 8.1 Hz, 2 H, H⁸), 4.89 (ddt, J_{HH} = 17.6 Hz, J_{HH} = 2.0 Hz, J_{HH} = 1.1 Hz, 2 H, *cis*-H⁹), 4.88 (ddt, J_{HH} = 9.5 Hz, J_{HH} = 2.0 Hz, J_{HH} = 1.1 Hz, 2 H, *trans*-H⁹), 1.84 (dt, J_{HH} = 8.1 Hz, J_{HH} = 1.1 Hz, 4 H, H⁷), 0.34 (s, 3 H, H⁶). ¹³C{¹H} NMR (CDCl₃): δ = 192.4 (1 C¹), 145.5 (1 C⁵), 136.7 (1 C²), 134.4 (2 C⁴), 133.4 (2 C⁸), 128.5 (2 C³), 114.4 (2 C⁹), 21.2 (2 C⁷), −6.1 (1 C⁶). ²⁹Si{¹H} NMR (CDCl₃): δ = −5.0. ESI-TOF: m/z = 231.10 [M + H]⁺ (calcd 231.12). Anal. calcd for C₁₄H₁₈OSi (230.38): C, 72.99; H, 7.88. Found: C, 72.54; H, 7.51.

meso-Tetrakis(4-allyldimethylsilylphenyl)porphyrin (3b)

To aldehyde **2b** (6.00 mmol, 1.224 g) and pyrrole (6.00 mmol, 0.403 g, 0.416 mL) dissolved in CH₂Cl₂ (600 mL), [BF₃·OEt₂] (0.60 mmol, 0.085 g, 0.076 mL) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and then 2,3-dichloro-5,6-dicyanobenzoquinone (4.50 mmol, 1.224 g) was added in a single portion and stirring was continued for 1 h. The reaction mixture was washed with saturated NaHCO₃ (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 obtained solid material was purified by column chromatography (a) ⁿhexane and (b) 20 vol% CH₂Cl₂–ⁿhexane. Porphyrin **3b** was obtained as a dark red solid (0.44 mmol, 0.44 g, 29% based on **2b**).

Mp = 350 °C (dec). IR (KBr disc): $\tilde{\nu}$ = 3315 (s, NH), 3069, 3056, 3011, 2994, 2911, 2880, 1627 (w, C=C), 1251 (m, CH₃ bending), 834, 818, 804 (s, SiC). ¹H NMR (CDCl₃): δ = 8.87 (s, 8 H, H¹), 8.23 (brd, J_{HH} = 7.9 Hz, 8 H, H⁵), 7.90 (brd, J_{HH} = 7.9 Hz, 8 H, H⁶), 6.01 (ddt, J_{HH} = 17.0 Hz, J_{HH} = 10.1 Hz, J_{HH} = 8.1 Hz, 4 H, H¹⁰), 5.04 (ddt, J_{HH} = 17.0 Hz, J_{HH} = 2.4 Hz, J_{HH} =

1.1 Hz, 4 H, *cis*-H¹¹), 5.01 (ddt, J_{HH} = 10.1 Hz, J_{HH} = 2.4 Hz, J_{HH} = 1.1 Hz, 3 H, *trans*-H¹¹), 2.02 (dt, J_{HH} = 8.1 Hz, J_{HH} = 1.1 Hz, 16 H, H⁹), 0.54 (s, 24 H, H⁸), −2.74 (brs, 2 H, NH). ¹³C{¹H} NMR (CDCl₃): δ = 142.8 (4 C⁷), 137.8 (4 C⁴), 134.7 (4 C¹⁰), 134.1 (8 C⁶), 132.0 (8 C⁵), 131.2 (br, 8 C¹), 120.1 (4 C³), 113.6 (4 C¹¹), 24.0 (4 C⁹), −3.2 (8 C⁸). ²⁹Si{¹H} NMR (CDCl₃): δ = −4.1. ESI-TOF: m/z = 1007.49 [M + H]⁺ (calcd 1007.48). Anal. calcd for C₆₄H₇₀N₄Si₄ (1007.61): C, 76.29; H, 7.00; N, 5.56. Found: C, 76.03; H, 7.26; N, 5.30.

meso-Tetrakis(4-diallylmethylsilylphenyl)porphyrin (3c)

To aldehyde **2c** (10.00 mmol, 2.301 g) and pyrrole (10.00 mmol, 0.671 g, 0.69 mL) dissolved in CH₂Cl₂ (1000 mL) [BF₃·OEt₂] (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-dicyanobenzoquinone (7.50 mmol, 1.703 g) was added in a single portion and stirring was continued for 1 h. The reaction mixture was washed with saturated NaHCO₃ (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) ⁿhexane and (b) 20 vol% CH₂Cl₂–ⁿhexane. 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, CH₃ bending), 800 (s, SiC). ¹H NMR (CDCl₃): δ = 8.90 (s, 8 H, H¹), 8.26 (brd, J_{HH} = 7.9 Hz, 8 H, H⁵), 7.92 (brd, J_{HH} = 7.9 Hz, 8 H, H⁶), 6.04 (ddt, J_{HH} = 17.0 Hz, J_{HH} = 10.1 Hz, J_{HH} = 8.1 Hz, 8 H, H¹⁰), 5.10 (ddt, J_{HH} = 17.0 Hz, J_{HH} = 2.0 Hz, J_{HH} = 0.9 Hz, 8 H, *cis*-H¹¹), 5.06 (ddt, J_{HH} = 10.1 Hz, J_{HH} = 2.0 Hz, J_{HH} = 0.9 Hz, 8 H, *trans*-H¹¹), 2.10 (dt, J_{HH} = 8.0 Hz, J_{HH} = 0.9 Hz, 32 H, H⁹), 0.58 (s, 24 H, H⁸), −2.69 (brs, 2 H, NH). ¹³C{¹H} NMR (CDCl₃): δ = 142.9 (4 C⁷), 136.1 (4 C⁴), 134.3 (8 C¹⁰), 134.1 (8 C⁶), 132.3 (8 C⁵), 131.1 (br, 8 C¹), 120.1 (4 C³), 114.1 (8 C¹¹), 21.8 (8 C⁹), −5.6 (4 C⁸). ²⁹Si{¹H} NMR (CDCl₃): δ = −5.2. ESI-TOF: m/z = 1111.50 [M + H]⁺ (calcd 1111.54). Anal. calcd for C₇₂H₇₈N₄Si₄ (1111.53): C, 77.78; H, 7.07; N, 5.04. Found: C, 77.68; H, 6.59; N, 4.80.

meso-Tetrakis(4-allyldimethylsilylphenyl)porphyrinato zinc (4a)

To **3b** (0.050 mmol, 0.0504 g) dissolved in CHCl₃ (15 mL), a MeOH solution (10 mL) containing [Zn(OAc)₂·2H₂O] (0.100 mmol, 0.0219 g) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and was then washed with saturated NaHCO₃ (15 mL) followed by washing with water (2 × 15 mL). The organic layer was dried over Na₂SO₄. 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, CH₃ bending), 836, 820, 811, 796 (s, SiC). ¹H NMR (CDCl₃): δ = 9.00 (s, 8 H, H¹), 8.25 (brd, J_{HH} = 7.9 Hz, 8 H, H⁵), 7.90 (brd, J_{HH} = 7.9 Hz, 8 H, H⁶), 6.02 (ddt, J_{HH} = 17.0 Hz, J_{HH} = 10.1 Hz, J_{HH} = 8.1 Hz, 4 H,



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^9), 0.56 (s, 24 H, H^8). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 150.2$ (4 C^2), 143.4 (4 C^7), 137.5 (4 C^4), 134.8 (4 C^{10}), 133.9 (8 C^6), 132.1 (8 C^1), 131.8 (8 C^5), 121.2 (4 C^3), 113.6 (4 C^{11}), 24.0 (4 C^9), -3.2 (8 C^8). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta = -4.1$ (4 Si). ESI-TOF: $m/z = 1070.44$ [M] $^+$ (calcd 1070.40). Anal. calcd for $C_{64}H_{70}N_4Si_4Zn$ (1073.00): C, 71.64; H, 6.58; N, 5.22. Found: C, 71.44; H, 6.58; N, 4.98.

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

To porphyrin **3c** (0.050 mmol, 0.0556 g) dissolved in $CHCl_3$ (15 mL), $[Zn(OAc)_2 \cdot 2H_2O]$ (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_2SO_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**).

$Mp = 350$ °C (dec). IR (KBr disc): $\tilde{\nu} = 3070, 3056, 3008, 2990, 2966, 2952, 2912, 2876, 1628$ (m, C=C), 1252 (m, $SiCH_3$ bending), 820 (s, SiC), 798 (s, SiC). 1H NMR ($CDCl_3$): $\delta = 8.98$ (s, 8 H, H^1), 8.24 (brd, $J_{HH} = 7.9$ Hz, 8 H, H^5), 7.89 (brd, $J_{HH} = 7.9$ Hz, 8 H, H^6), 6.01 (ddt, $J_{HH} = 17.0$ Hz, $J_{HH} = 10.1$ Hz, $J_{HH} = 8.1$ Hz, 8 H, H^{10}), 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^9), 0.55 (s, 12 H, H^8). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 150.1$ (4 C^2), 143.6 (4 C^7), 135.8 (4 C^4), 134.3 (8 C^{10}), 133.9 (8 C^6), 132.2 (8 C^5), 132.0 (8 C^1), 121.1 (4 C^3), 114.1 (8 C^{11}), 21.9 (8 C^9), -5.6 (4 C^8). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta = -5.2$. ESI-TOF: $m/z = 1174.48$ [M] $^+$ (calcd 1174.46). Anal. calcd for $C_{72}H_{78}N_4Si_4Zn$ (1177.15): C, 73.46; H, 6.68; N, 4.76. Found: C, 73.24; H, 6.45; N, 4.68.

meso-Tetrakis[4-dimethyl(3-hydroxypropyl)silylphenyl]porphyrin (5a)

To $[BH_3 \cdot SMe_2]$ (2.0 M, 2.00 mmol, 1.00 mL) dissolved in thf (5.0 mL), **3b** (0.397 mmol, 0.400 g) in thf (30 mL) was drop-wise added over 10 min at 0 °C. The reaction solution was stirred for 2 h at this temperature and afterwards it was quenched with aqueous NaOH (3 M, 0.75 mL) and stirring was continued for 15 min. Afterwards, H_2O_2 (30%, 0.75 mL) was added in a single portion, stirring was continued at ambient temperature for 30 min and then the reaction mixture was extracted with saturated aqueous K_2CO_3 (20 mL) and with a Et_2O -thf mixture (ratio 1 : 1, v/v; 50 mL). The organic layer was washed with brine and filtered through a silica gel column (thf, column size 1.0 \times 10 cm). From the eluate, all volatiles were removed in oil-pump vacuum and the residue was washed with Et_2O (3×15 mL) and was then dried in oil-pump vacuum to give **5a** (0.332 mmol, 0.358 g, 83% based on **3b**) as a dark red solid.

$Mp = 350$ °C (dec). IR (KBr disc): $\tilde{\nu} = 3397$ (s, OH), 3314 (s, NH), 3055, 3011, 2994, 2926, 2864, 1251 (m, CH_3 bending),

833, 803 (s, SiC). 1H NMR ($dmsO-d_6$): $\delta = 8.85$ (s, 8 H, H^1), 8.23 (d, $J_{HH} = 7.4$ Hz, 8 H, H^5), 7.96 (d, $J_{HH} = 7.3$ Hz, 8 H, H^6), 4.53 (t, $J_{HH} = 5.3$ Hz, 4 H, OH), 3.51 (q, $J_{HH} = 6.2$ Hz, 8 H, H^{11}), 1.67 (m, 8 H, H^{10}), 0.96 (m, 8 H, H^9), 0.50 (s, 24 H, H^8), -2.87 (br, 2 H, NH). 1H NMR (thf- d_8): $\delta = 8.84$ (s, 8 H, H^1), 8.22 (d, $J_{HH} = 7.8$ Hz, 8 H, H^5), 7.95 (d, $J_{HH} = 7.8$ Hz, 8 H, H^6), 3.58 (t, $J_{HH} = 6.2$ Hz, 8 H, H^{11}), 1.64 (m, 8 H, H^{10}), 1.03 (m, 8 H, H^9), 0.52 (s, 24 H, H^8). $^{13}C\{^1H\}$ NMR (thf- d_8): $\delta = 143.6$ (4 C^7), 139.4 (4 C^4), 134.8 (8 C^6), 132.7 (8 C^5), 131.7 (br, 8 C^1), 120.9 (4 C^3), 65.5 (4 C^{11}), 28.5 (4 C^{10}), 12.5 (4 C^9), -2.8 (8 C^8). $^{29}Si\{^1H\}$ NMR ($dmsO-d_6$): $\delta = -2.0$. $^{29}Si\{^1H\}$ NMR (thf- d_8): $\delta = -4.0$. ESI-TOF: $m/z = 1079.60$ [$M + H$] $^+$ (calcd 1079.52). Anal. calcd for $C_{64}H_{78}N_4O_4Si_4$ (1150.57): C, 70.91; H, 7.53; N, 4.86. Found: C, 70.63; H, 7.65; N, 4.98.

meso-Tetrakis[4-methyldi(3-hydroxypropyl)silylphenyl]porphyrin (5b)

To $[BH_3 \cdot SMe_2]$ (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_2O_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_2CO_3 (20 mL) and then with a Et_2O -thf mixture (ratio 1 : 1, v/v; 50 mL). The organic layer was washed with brine and filtered through silica gel (thf, column size 1 \times 10 cm). All volatiles were removed in oil-pump vacuum and the residue was washed with Et_2O (3×15 mL) and then dried in oil-pump vacuum to give **5b** as a dark red solid (0.150 mmol, 0.186 g, 72% based on **3c**).

$Mp = 350$ °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). 1H NMR ($dmsO-d_6$): $\delta = 8.87$ (s, 8 H, H^1), 8.26 (d, $J_{HH} = 7.5$ Hz, 8 H, H^5), 7.97 (d, $J_{HH} = 7.5$ Hz, 8 H, H^6), 4.56 (t, $J_{HH} = 5.3$ Hz, 8 H, OH), 3.51 (q, $J_{HH} = 6.1$ Hz, 16 H, H^{11}), 1.67 (m, 16 H, H^{10}), 1.00 (m, 16 H, H^9), 0.51 (s, 12 H, H^8), -2.86 (br, 2 H, NH). 1H NMR (thf- d_8): $\delta = 8.84$ (s, 8 H, H^1), 8.22 (d, $J_{HH} = 7.6$ Hz, 8 H, H^5), 7.96 (d, $J_{HH} = 7.6$ Hz, 8 H, H^6), 3.58 (t, $J_{HH} = 6.4$ Hz, 16 H, H^{11}), 1.74 (m, 16 H, H^{10}), 1.06 (m, 16 H, H^9), 0.52 (s, 12 H, H^8). $^{13}C\{^1H\}$ NMR (thf- d_8): $\delta = 143.5$ (4 C^7), 138.6 (4 C^4), 134.8 (8 C^6), 133.1 (8 C^5), 131.7 (br, 8 C^1), 121.0 (4 C^3), 65.6 (8 C^{11}), 28.5 (8 C^{10}), 10.9 (4 C^9), -4.8 (8 C^8). $^{29}Si\{^1H\}$ NMR ($dmsO-d_6$): $\delta = -0.8$. $^{29}Si\{^1H\}$ NMR (thf- d_8): $\delta = -0.8$. ESI-TOF: $m/z = 1293.70$ [$M + K$] $^+$ (calcd 1293.58). Anal. calcd for $C_{72}H_{94}N_4O_8Si_4 \cdot H_2O$ (1273.90): C, 67.88; H, 7.60; N, 4.40. Found: C, 67.68; H, 7.65; N, 4.31.

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

To **5a** (0.0926 mmol, 0.100 g) dissolved in thf (30 mL) a solution of $[Zn(OAc)_2 \cdot 2H_2O]$ (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-*n*-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, 0.0980 g, 93% based on **5a**).

Mp = 350 °C (dec). IR (KBr disc): $\tilde{\nu}$ = 3398 (m, OH), 3048, 3004, 2945, 2927, 2863, 1246 (s, CH₃ bending), 831, 798 (s, SiC). ¹H NMR (dmsO-*d*₆): δ = 8.76 (s, 8 H, H¹), 8.16 (d, *J*_{HH} = 7.5 Hz, 8 H, H⁵), 7.89 (d, *J*_{HH} = 7.5 Hz, 8 H, H⁶), 4.49 (t, *J*_{HH} = 6.2 Hz, 4 H, OH), 3.46 (q, *J*_{HH} = 6.3 Hz, 8 H, H¹¹), 1.63 (m, 8 H, H¹⁰), 0.92 (m, 8 H, H⁹), 0.47 (s, 24 H, H⁸). ¹³C{¹H} NMR (dmsO-*d*₆): δ = 150.1 (4 C²), 144.2 (4 C⁷), 138.6 (4 C⁴), 134.7 (8 C⁶), 132.6 (8 C⁵ and 8 C¹), 121.2 (4 C³), 64.8 (4 C¹¹), 28.2 (4 C¹⁰), 12.4 (4 C⁹), -1.8 (8 C⁸). ²⁹Si{¹H} NMR (dmsO-*d*₆): δ = -2.1. ESI-TOF: *m/z* = 1179.50 [M + K]⁺ (calcd 1179.39). Anal. calcd for C₆₄H₇₆N₄O₄Si₄Zn (1143.04): C, 67.25; H, 6.70; N, 4.90. Found: C, 67.44; H, 7.12; N, 4.81.

meso-Tetrakis[4-methyldi(3-hydroxypropyl)silylphenyl]-porphyrinato 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**).

Mp = 350 °C (dec). IR (KBr disc): $\tilde{\nu}$ = 3403 (m, OH), 3055, 3004, 2923, 2863, 1250 (w, CH₃ bending), 858, 796 (s, SiC). ¹H NMR (dmsO-*d*₆): δ = 8.77 (s, 8 H, H¹), 8.18 (d, *J*_{HH} = 7.7 Hz, 8 H, H⁵), 7.90 (d, *J*_{HH} = 7.7 Hz, 8 H, H⁶), 4.49 (t, *J*_{HH} = 6.2 Hz, 8 H, OH), 3.46 (q, *J*_{HH} = 6.3 Hz, 8 H, H¹¹), 1.64 (m, 16 H, H¹⁰), 0.95 (m, 16 H, H⁹), 0.47 (s, 12 H, H⁸). ¹³C{¹H} NMR (dmsO-*d*₆): δ = 150.2 (4 C²), 144.2 (4 C⁷), 137.8 (4 C⁴), 134.8 (8 C⁶), 132.9 (8 C⁵), 132.6 (br, 8 C¹), 121.3 (4 C³), 64.9 (4 C¹¹), 28.2 (4 C¹⁰), 10.8 (4 C⁹), -3.8 (8 C⁸). ²⁹Si{¹H} NMR (dmsO-*d*₆): δ = -0.9. ESI-TOF: *m/z* = 1355.62 [M + K]⁺ (calcd 1355.49). Anal. calcd for C₇₂H₉₂N₄O₈Si₄Zn (1319.24): C, 65.33; H, 6.95; N, 4.29. Found: C, 64.89; H, 7.11; N, 4.07.

4-[Tris(4-trimethylsilylphenyl)silyl]benzaldehyde (8a)

The synthetic procedure described for the preparation of **2b** (see earlier) was applied to synthesize **8a**: ^tBuLi (1.7 M, 13.00 mmol, 7.70 mL, *n*-pentane), **7a** (6.50 mmol, 4.10 g) in Et₂O (70 mL), dimethyl formamide (19.50 mmol, 1.43 g, 1.51 mL) in thf (40 mL) and aqueous HCl (3 N, 40 mL). After appropriate work-up, **8a** could be isolated as a colorless solid (5.93 mmol, 3.45 g, 91% based on **7a**).

Mp = 212 °C. IR (film): $\tilde{\nu}$ = 3048, 2996, 2953 (m), 2894, 2816 (w, CHO), 2722 (w, CHO), 1706 (s, C=O), 1249 (w, CH₃ bending), 1133, 838 (s, SiC). ¹H NMR (CDCl₃): δ = 10.06 (s, 1 H, CHO), 7.87 (brd, *J*_{HH} = 8.2 Hz, 2 H, H³), 7.78 (brd, *J*_{HH} = 8.2 Hz, 2 H, H⁴), 7.55 (s, 12 H, H⁷ and H⁸), 0.29 (s, 27 H, H¹⁰). ¹³C{¹H} NMR (CDCl₃): δ = 192.6 (1 C¹), 143.2 (1 C²), 142.4 (3 C⁹), 136.9 (2 C⁴), 135.5 (6 C⁷), 133.5 (3 C⁶), 132.8 (6 C⁸), 128.6 (2 C³), 127.8 (1 C⁵), -1.2 (9 C¹⁰). ²⁹Si{¹H} NMR (CDCl₃): δ = -14.7 (1 Si¹), -3.9 (3 Si²). ESI-TOF: *m/z* = 619.24 [M + K]⁺ (calcd 619.21). Anal. calcd for C₃₅H₄₄OSi₄ (581.05): C, 70.28; H, 7.63. Found: C, 70.19; H, 7.45.

NMR (CDCl₃): δ = 192.6 (1 C¹), 143.2 (1 C²), 142.4 (3 C⁹), 136.9 (2 C⁴), 135.5 (6 C⁷), 133.5 (3 C⁶), 132.8 (6 C⁸), 128.6 (2 C³), 127.8 (1 C⁵), -1.2 (9 C¹⁰). ²⁹Si{¹H} NMR (CDCl₃): δ = -14.7 (1 Si¹), -3.9 (3 Si²). ESI-TOF: *m/z* = 619.24 [M + K]⁺ (calcd 619.21). Anal. calcd for C₃₅H₄₄OSi₄ (581.05): C, 70.28; H, 7.63. Found: C, 70.19; H, 7.45.

4-[Tris(4-diallylmethylsilylphenyl)silyl]benzaldehyde (8c)

The same procedure as described for preparing **2b** was applied in the synthesis of **8c** (see above): ^tBuLi (1.7 M, 6.00 mmol, 3.60 mL, *n*-pentane), **7c** (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 **7c**).

IR (film): $\tilde{\nu}$ = 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, H³), 7.77 (brd, *J*_{HH} = 8.1 Hz, 2 H, H⁴), 7.55 (brs, 12 H, H⁷ and H⁸), 5.80 (ddt, *J*_{HH} = 16.9 Hz, *J*_{HH} = 10.2 Hz, *J*_{HH} = 8.0 Hz, 6 H, H¹²), 4.91 (ddt, *J*_{HH} = 16.9 Hz, *J*_{HH} = 2.1 Hz, *J*_{HH} = 1.1 Hz, 6 H, *cis*-H¹³), 4.89 (ddt, *J*_{HH} = 10.2 Hz, *J*_{HH} = 2.1 Hz, *J*_{HH} = 1.1 Hz, 6 H, *trans*-H¹³), 1.84 (brd, *J*_{HH} = 8.0 Hz, 12 H, H¹¹), 0.31 (s, 9 H, H¹⁰). ¹³C{¹H} NMR (CDCl₃): δ = 192.5 (1 C¹), 142.8 (1 C²), 139.1 (3 C⁹), 137.0 (1 C⁵), 136.9 (2 C⁴), 135.4 (6 C⁸), 134.0 (6 C¹²), 133.9 (3 C⁶), 133.4 (6 C⁷), 128.6 (2 C³), 113.5 (6 C¹³), 23.5 (6 C¹¹), -3.6 (3 C¹⁰). ²⁹Si{¹H} NMR (CDCl₃): δ = -14.7 (1 Si¹), -5.7 (3 Si²). ESI-TOF: *m/z* = 775.01 [M + K]⁺ (calcd 775.30). Anal. calcd for C₄₆H₅₆OSi₄ (737.28): C, 74.94; H, 7.66. Found: C, 74.93; H, 7.77.

meso-Tetrakis{4-[tris(4-trimethylsilylphenyl)silyl]phenyl}-porphyrin (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-dicyanobenzoquinone (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) *n*-hexane and (b) 20 vol% CH₂Cl₂-*n*-hexane. After all volatiles were removed in oil pump vacuum, porphyrin **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): $\tilde{\nu}$ = 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, H¹), 8.27 (brd, *J*_{HH} = 8.0 Hz, 8 H, H⁵), 8.02 (brd, *J*_{HH} = 8.0 Hz, 8 H, H⁶), 7.85 (brd, *J*_{HH} = 8.0 Hz, 24 H, H⁹), 7.70 (brd, *J*_{HH} = 8.0 Hz, 24 H, H¹⁰), 0.36 (s, 108 H, H¹²), -2.72 (br, 2 H, NH). ¹³C{¹H} NMR (CDCl₃): δ = 143.3 (4 C⁴), 142.2 (12 C¹¹), 135.8 (24 C¹⁰), 134.7 (8 C⁶), 134.6 (12 C⁸), 134.2 (8 C⁵), 133.5 (4 C⁷) 132.9



(24 C⁹), 120.1 (4 C³), −1.1 (36 C¹²). ²⁹Si{¹H} NMR (CDCl₃): δ = −14.2 (4 Si¹), −4.5 (12 Si²). Anal. calcd for C₁₅₂H₁₈₂N₄Si₁₆ (2514.47): C, 72.60; H, 7.30; N, 2.23. Found: C, 72.54; H, 6.93; N, 2.13.

meso-Tetrakis{4-[tris(4-diallylmethylsilylphenyl)silyl]phenyl}-porphyrin (9c)

To **8c** (1.81 mmol, 1.333 g) and pyrrole (1.81 mmol, 0.122 g, 0.13 mL) dissolved in CH₂Cl₂ (180 mL), [BF₃·OEt₂] (0.18 mmol, 0.026 g, 0.02 mL) was added in a single portion. The reaction solution was stirred for 2 h and then 2,3-dichloro-5,6-dicyanobenzoquinone (1.36 mmol, 0.308 g) was added and stirring was continued for 1 h. The reaction mixture was washed with saturated NaHCO₃ (40 mL) and then with water (3 × 40 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) ⁿhexane and (b) 20 vol% CH₂Cl₂–ⁿhexane. After removal of all volatiles in a vacuum, porphyrin **9c** was isolated as a dark red solid (0.143 mmol, 0.452 g, 32% based on **8c**).

Mp = 350 °C (dec). IR (KBr disc): $\tilde{\nu}$ = 3322 (S, NH), 3074, 3050, 2996, 2968, 2954, 2912, 2878, 1630 (m, C=C), 1252 (m, CH₃ bending), 1132, 822 (s, SiC), 802 (s, SiC). ¹H NMR (CDCl₃): δ = 8.94 (s, 8 H, H¹), 8.28 (brd, *J*_{HH} = 7.6 Hz, 8 H, H⁵), 7.99 (brd, *J*_{HH} = 7.6 Hz, 8H, H⁶), 7.82 (brd, *J*_{HH} = 7.5 Hz, 24 H, H⁹), 7.68 (brd, *J*_{HH} = 7.5 Hz, 24 H, H¹⁰), 5.86 (ddt, *J*_{HH} = 17.2 Hz, *J*_{HH} = 9.6 Hz, *J*_{HH} = 8.1 Hz, 24 H, H¹⁴), 4.95 (brd, *J*_{HH} = 17.2 Hz, 24 H, *cis*-H¹⁵), 4.93 (brd, 9.6 Hz, 24 H, *trans*-H¹⁵), 1.90 (brd, 8.00 Hz, 48 H, H¹³), 0.37 (s, 36 H, H¹²), −2.75 (s, 2 H, NH). ¹³C{¹H} NMR (CDCl₃): δ = 143.4 (4 C⁴), 138.9 (12 C¹¹), 135.7 (24 C¹⁰), 135.0 (12 C⁸), 134.8 (8 C⁶), 134.3 (8 C⁵), 134.2 (24 C¹⁴), 133.5 (24 C⁹), 133.2 (4 C⁷), 120.1 (4 C³), 114.0 (24 C¹⁵), 21.6 (24 C¹³), −5.8 (24 C¹²). ²⁹Si{¹H} NMR (CDCl₃): δ = −14.2 (4 Si¹), −5.7 (12 Si²). Anal. calcd for C₂₀₀H₂₃₀N₄Si₁₆ (3153.39): C, 76.52; H, 7.38, N, 1.78. Found: C, 76.66; H, 7.17; N, 1.23.

meso-Tetrakis{4-[tris(4-trimethylsilylphenyl)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) in MeOH (2.5 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 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): $\tilde{\nu}$ = 3046, 2994, 2952, 2932, 2893, 1249 (m, CH₃ bending), 1132, 845 (s, SiC), 839 (s, SiC), 803. ¹H NMR (CDCl₃): δ = 9.02 (s, 8 H, H¹), 8.25 (brd, *J*_{HH} = 7.9 Hz, 8 H, H⁵), 7.99 (brd, *J*_{HH} = 7.9 Hz, 8 H, H⁶), 7.83 (brd, *J*_{HH} = 7.8 Hz, 24 H, H⁹), 7.68 (brd, *J*_{HH} = 7.8 Hz, 24 H, H¹⁰), 0.34 (s, 108 H, H¹²). ¹³C{¹H} NMR (CDCl₃): δ = 150.1 (8 C²), 144.0 (4 C⁴), 142.1 (12 C¹¹), 135.8 (24 C¹⁰), 134.7 (12 C⁸), 134.6 (8 C⁶), 134.1 (8 C⁵), 133.2 (4 C⁷), 132.9 (24 C⁹), 132.1 (8 C¹),

121.1 (4 C³), −1.1 (36 C¹²). ²⁹Si{¹H} NMR (CDCl₃): δ = −14.3 (4 Si¹), −3.9 (12 Si²). Anal. calcd for C₁₅₂H₁₈₀N₄Si₁₆Zn·EtOH (2619.02): C, 70.49; H, 7.14; N, 2.14. Found: C, 70.51; H, 6.95; N, 1.86.

meso-Tetrakis{4-[tris(4-allyldimethylsilylphenyl)silyl]phenyl}-porphyrinato zinc (10b)

To **9b** (0.0123 mmol, 0.0350 g) dissolved in CHCl₃ (5 mL), [Zn(OAc)₂·2H₂O] (0.0308 mmol, 0.0067 g) in MeOH (2.5 mL) was added in a single portion. The reaction solution was stirred for 2 h at ambient temperature and then 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 **10b** as a dark red solid (0.0118 mmol, 0.336 g, 96% based on **9b**).

Mp = 350 °C (dec). IR (KBr disc): $\tilde{\nu}$ = 3074, 3047, 2994, 2953, 2912, 1628 (m, C=C), 1249 (m, CH₃ bending), 1132, 835 (s, SiC), 799 (s, SiC). ¹H NMR (CDCl₃): δ = 9.05 (s, 8 H, H¹), 8.29 (brd, *J*_{HH} = 8.0 Hz, 8 H, H⁵), 7.97 (brd, *J*_{HH} = 8.0 Hz, 8H, H⁶), 7.85 (brd, *J*_{HH} = 8.0 Hz, 24 H, H⁹), 7.70 (brd, *J*_{HH} = 8.0 Hz, 24 H, H¹⁰), 5.88 (ddt, *J*_{HH} = 16.9 Hz, *J*_{HH} = 10.2 Hz, *J*_{HH} = 8.1 Hz, 24 H, H¹⁴), 4.95 (ddt, *J*_{HH} = 16.9 Hz, *J*_{HH} = 2.1 Hz, *J*_{HH} = 1.1 Hz, *cis*-H¹⁵), 4.92 (ddt, *J*_{HH} = 10.2 Hz, *J*_{HH} = 2.1 Hz, *J*_{HH} = 1.1 Hz, *trans*-H¹⁵), 1.86 (dt, *J*_{HH} = 8.1 Hz, *J*_{HH} = 1.1 Hz, 24 H, H¹³), 0.38 (s, 72 H, H¹²). ¹³C{¹H} NMR (CDCl₃): δ = 150.1 (8 C²), 144.0 (4 C⁴), 140.5 (12 C¹¹), 135.8 (24 C¹⁰), 134.9 (12 C⁸), 134.6 (12 C¹⁴ and 8 C⁶), 134.1 (8 C⁵), 133.2 (24 C⁹), 133.0 (4 C⁷), 132.1 (8 C¹), 121.1 (4 C³), 113.5 (12 C¹⁵), 23.6 (12 C¹³), −3.5 (24 C¹²). ²⁹Si{¹H} NMR (CDCl₃): δ = −14.2 (4 Si¹), −4.5 (12 Si²). Anal. calcd for C₁₇₆H₂₀₄N₄Si₁₆Zn·2EtOH (2982.26): 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** (0.0308 mmol, 0.099 g, 97% based on **9c**).

Mp = 350 °C (dec). IR (KBr disc): $\tilde{\nu}$ = 3074, 3050, 2994, 2968, 2912, 2878, 1628 (m, C=C), 1252 (m, CH₃ bending), 1132, 820 (s, SiC), 802 (s, SiC). ¹H NMR (CDCl₃): δ = 9.03 (s, 8 H, H¹), 8.27 (brd, *J*_{HH} = 8.0 Hz, 8 H, H⁵), 7.97 (brd, *J*_{HH} = 8.0 Hz, 8H, H⁶), 7.82 (brd, *J*_{HH} = 8.0 Hz, 24 H, H⁹), 7.67 (brd, *J*_{HH} = 8.0 Hz, 24 H, H¹⁰), 5.85 (ddt, *J*_{HH} = 16.9 Hz, *J*_{HH} = 9.6 Hz, *J*_{HH} = 8.1 Hz, 24 H, H¹⁴), 4.94 (ddt, *J*_{HH} = 16.9 Hz, *J*_{HH} = 2.1 Hz, *J*_{HH} = 1.0 Hz, *cis*-H¹⁵), 4.91 (ddt, *J*_{HH} = 9.9 Hz, *J*_{HH} = 2.1 Hz, *J*_{HH} = 1.0 Hz, *trans*-H¹⁵), 1.89 (brd, *J*_{HH} = 8.1 Hz, 48 H, H¹³), 0.36 (s, 36 H, H¹²). ¹³C{¹H} NMR (CDCl₃): δ = 150.1 (8 C²), 144.1 (4C⁴), 138.8 (12 C¹¹), 135.7 (24 C¹⁰), 135.1 (12 C⁸), 134.6 (8 C⁶), 134.2 (24 C¹⁴), 134.1 (8 C⁵), 133.5 (24 C⁹), 132.9 (4 C⁷), 132.1 (8 C¹),



121.1 (4 C³), 114.0 (24 C¹⁵), 21.6 (24 C¹³), −5.8 (12 C¹²). ²⁹Si {¹H} NMR (CDCl₃): δ = −14.2 (4 Si¹), −5.7 (12 Si²). Anal. calcd for C₂₀₀H₂₂₈N₄Si₁₆Zn·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 K_α radiation (λ = 0.71073 Å), while for data collection of **6a** an Oxford Gemini S diffractometer and Cu K_α 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 SHELXS-97 and refined by full-matrix least-squares procedures on F² using the SHELXL-97 as part of the software package SHELXTL.⁴⁶ 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 (C11O, 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_{ij} values. Due to that it appears less trustworthy to assign for them π - π interactions correctly apart from attractive van der Waals forces.



40 (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 C01--–C83--

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

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