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Self-Assembly and Chiroptical Properties of Chiral Dendrimers Consisting of a Hamilton Receptor Substituted Porphyrin and Depsipeptide Cyanurates

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The synthesis and characterisation of a new type of porphyrin-based tetrakis(Hamilton receptor) **1** is presented and the complexation of **1** with the chiral depsipeptide dendrons **7**–**12**, with cyanuric acid functionalities as their focal points, is reported. The resulting first- to third-generation chiral supramolecular dendrimers **13**–**18** were characterised by NMR, UV/Vis and CD spectroscopy. Chirality transfer from the depsipeptide dendrons to the porphyrin core was demonstrated by CD spectroscopy in the case of the second- and third-generation complexes **15**–**18**, whereas no chirality transfer and hence no diastereoselective formation of a chiral superstructure could be determined in the case of the first-generation systems. The intensities of the complexes' CD absorptions in the porphyrin region are inversely proportional to the size of the dendrons, pointing to a size-dependent cooperativity of the fourfold complexation of the dendrons with the more effective binding of the second-generation dendrons **9** and **10** relative to their bulkier third-generation counterparts **11** and **12**. Pronounced cooperativity during the formation of the second-generation **1**:$\mathbf{L_4}$ complexes (**L** = **9**, **10**) is considered to be the reason for the diastereoselective formation of a preferred chiral conformation of the Hamilton receptor **1** in the complexes **15** and **16**.

Introduction

The rather new area of supramolecular chirality[1] represents a combination of molecular chirality and supramolecular chemistry.[2] The self-assembly of chiral molecules[3] or assembly between chiral and achiral molecules through noncovalent interactions can result in the formation of chiral superstructures.[4] As a consequence, transfer of chiral information may not be restricted only to the induction of chirality in the achiral building blocks, but can also cause amplification of chirality in the whole supramolecular system.[5] Chirality at the supramolecular level, termed supramolecular chirogenesis,[6] is abundant in biology and plays an essential role in many natural systems. A large number of natural supramolecular structures are stabilised by interstrand hydrogen bonds: the DNA double helix[7] and its handedness, for example, are influenced by the configurations of chiral centres in the nucleotide backbone. Chiral dendrimers are considered to be appealing candidates for the investigation of chirality at the macromolecular level,[8] and amino acids and peptides have frequently been used as building blocks for the construction of chiral dendrimers.[9] Because of the biological importance of porphyrins, covalently linked porphyrin–dendrimer hybrids have been synthesised and studied as synthetic models for globular heme proteins.[10] Experiments have established that the electrochemical properties of the porphyrin core are considerably influenced by the size and type of the dendritic environment, and complexes of the dendritically functionalised Fe^{II} species of these systems, containing 1,2-dimethylimidazole (DiMeIm) as an axially coordinated ligand, have been investigated as model systems for T(tense)-state haemoglobin and myoglobin.[10c] The (porphyrin)Fe^{II} derivatives, containing secondary amide groups in their dendritic structures, showed stable and reversible complexation with O_2 and CO. The same dendrimer derivatives containing (porphyrin)Fe^{III} complexes as active site and imidazole as axial ligand were investigated as heme oxygenase model compounds.[10d] The catalytic activity of these systems, with respect to epoxidation of alkenes and oxidation of sulfides, was found to be independent of the size and character of the peptidic shell. Because of the instability of the iron core towards self-oxidation, these systems were found to be rather unsuitable as catalysts. (Porphyrin)zinc cores connected to different Fréchet-type dendrons have been intensively studied with respect to their fluorescence properties.[11] Their derivatisation with up to eight boron-dipyrrin pigments has been used to mimic natural photosynthetic antenna complexes.[12] Recently, we reported on a new class of chiral depsipeptide dendrons based on tartaric acid as a branching juncture and ω-aminocapronic acid as spacer units.[13–16] Investigations of the chiroptical properties of

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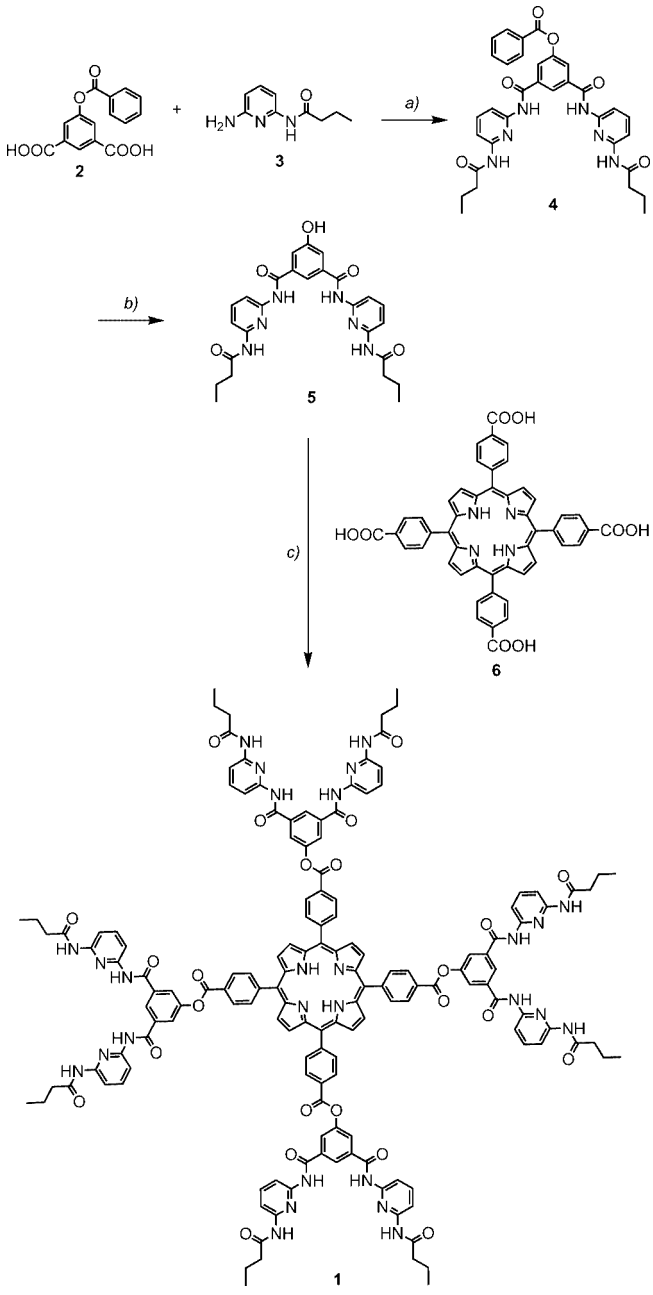
depsipeptide dendrons in different solvents showed that formation of chiral secondary structures in nonprotic solvents such as CH_3CN is possible.[14] In this context we also reported the synthesis, characterisation and chiroptical properties of chiral Ru^{II}-coordinated dendrimers.[15] Each chiral depsipeptide dendrimer was associated with a 2,2′-bipyridine core. Threefold coordination of these bipyridine ligands with Ru^{II} resulted in the formation of octahedral Δ- and Λ-configured diastereomers. Chiral depsipeptide dendrimers containing ethylenediaminetetraacetic acid (EDTA) ester derived cores have also been synthesized,[16] and chiroptical investigations on Zn^{II} and Cu^{II} complexes revealed metal-induced diastereoselective chiral folding of these systems. We have recently been developing the self-assembly of supramolecular dendrimers based upon the Hamilton receptor binding motif.[17] The biological importance and remarkable photoelectronic properties of porphyrins[18] have stimulated interest in the design and synthesis of dynamic supramolecular systems. Porphyrins functionalised with the Hamilton receptor coordination motif have been used as model compounds for the study of enzymatic molecular recognition[19] and for the construction of a noncovalent photoactive system.[20] We now report on the synthesis and chiroptical properties of a new porphyrin building block, containing four covalently bound Hamilton-type barbiturate or cyanurate receptors, and its complexation with chiral depsipeptide dendrons possessing cyanuric acid functionalities.

Results and Discussion

Synthesis of the Hamilton Receptor Substituted Porphyrin 1

The target porphyrin **1** was synthesised as shown in Scheme 1. Treatment of the diacid **2**[21] with thionyl chloride ($SOCl_2$) at reflux, followed by in situ coupling of the dichloride with the aminopyridine derivative **3**,[22] afforded the benzyl-protected Hamilton receptor **4** in 33% isolated yield. Deprotection of **4** with potassium hydroxide resulted in the formation of compound **5**, which was isolated in 61% yield. The solubility of the deprotected receptor **5** was limited to a few polar aprotic solvents such as tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and dioxane. The porphyrin tetraester **1** was obtained by fourfold esterification of the commercially available porphyrin-tetraacid **6** with **5** under *N*′-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide (EDC) coupling conditions, the reaction being performed in dry DMF with 4-(dimethylamino)-pyridine (DMAP) as a catalyst and the mixture stirred at room temp. for 7 d.

Because of its insolubility in most common organic solvents except for DMF, THF and DMSO, together with its high polarity, the purification of **1** was achieved by repeated column chromatography with different solvents [silica gel (SiO_2); THF, THF/dichloromethane (CH_2Cl_2), 80:20] followed by preparative HPLC (Nucleosil; THF/CH_2Cl_2, 80:20). The use of *N*,*N*′-dicyclohexylcarbodiimide (DCC) as coupling reagent is not recommended because the removal of the dicyclohexylurea by-product (DCU) turned out to be very difficult: even after repeated GPC column chromatography (SX-3000; DMF) the separation of the DCU by-product was not successful. It should be noted here that the formation of all possible porphyrin side products was observed by FAB-MS when either DCC or EDC were used in the esterification reaction. The target molecule **1** was characterized by ^1H and ^{13}C NMR, UV/Vis and IR spectroscopy and its expected molecular weight was confirmed by FAB mass spectrometry. The assignment of the ^1H NMR signals of the Hamilton receptor protons was carried out by analysis of the HETCOR and COSY spectra



Scheme 1. Synthesis of the Hamilton receptor substituted porphyrin **1**: a) $SOCl_2$, DMF, THF, room temperature, 16 h, 34%; b) KOH, dioxane, room temperature, 48 h, 61%; c) EDC, DMAP, DMF, room temperature, 7 d, 5%.

(Figure 1). In the range between δ = 0 and 3 ppm the COSY spectrum (Figure 1a) reveals the characteristic cross coupling pattern of the alkyl chain protons, which appear as a well-resolved multiplet and two triplet signals. The spectrum shows the expected coupling pattern of the aromatic protons of the pyridine fragment (16-H to 18-H) at δ ≈ 8 ppm. The HETCOR spectrum (Figure 1b) allowed assignment of the corresponding C atoms. The resonances of the porphyrin H atoms (21-H to 23-H) are located in the downfield region between δ = 8.6 and 9.3 ppm. The assignment of the C atoms was achieved by analysis of the correlation signals of the two characteristic doublets corresponding to 21-H and 22-H. The signals of the alkyl protons are located in the range between δ = 0.9 and 1.8 ppm,

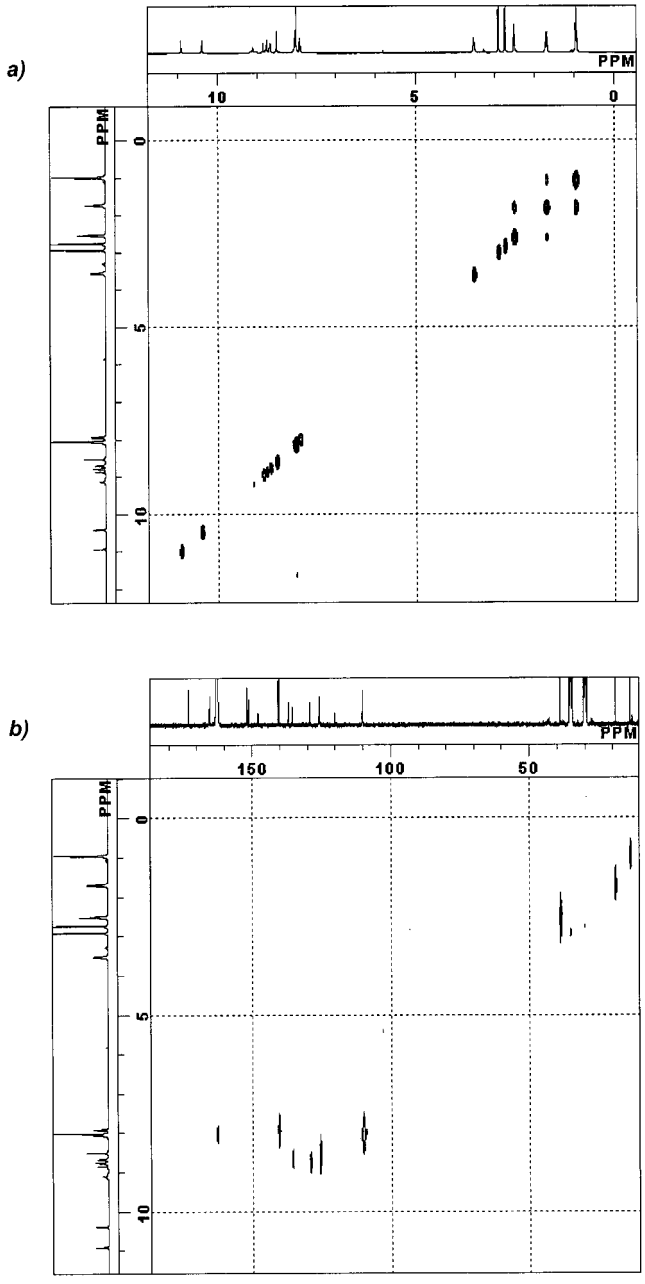


Figure 1. a) COSY and b) HETCOR NMR spectra of compound **1** (400 MHz, room temperature, [D_7]DMF).

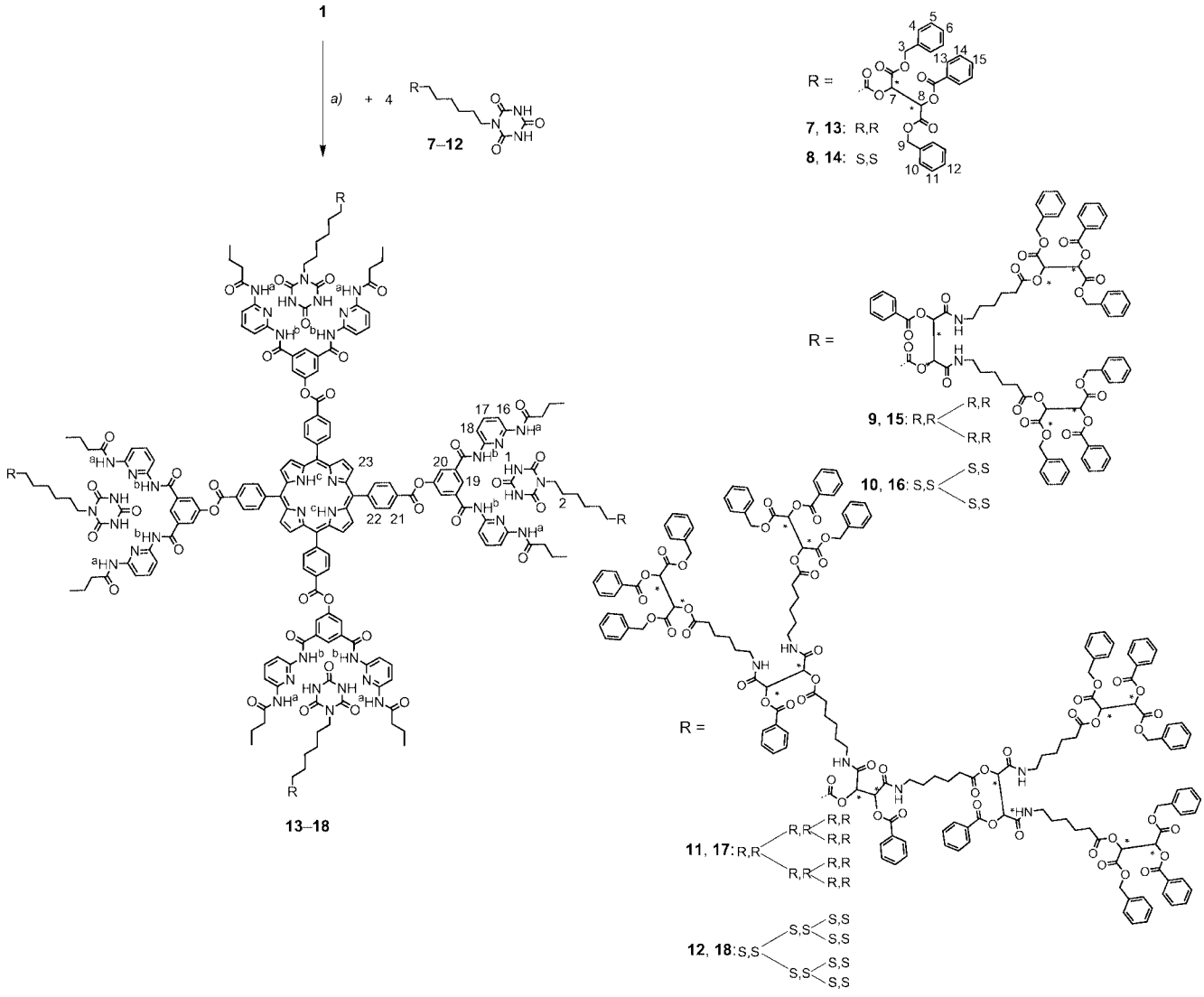
while the signals of the aromatic protons of the porphyrin and the Hamilton receptor unit can be observed between δ = 7.8 and 9.3 ppm. The signal of the aromatic protons 17-H appears at δ = 7.92 ppm as a triplet, while the resonances of 16-H and 18-H are covered by the signal of the solvent residual peak at δ = 8.0 ppm. At δ = 8.5 ppm the spectrum displays a sharp singlet, which can be assigned to the *ortho*-protons 20-H of the isophthalic unit. In the range between δ = 8.6 and 8.7 ppm the spectrum shows the two characteristic doublets of the aromatic protons 21-H and 22-H, followed by the singlet of the *para*-protons 19-H of the isophthalic unit. The β-pyrrolic protons 23-H resonate as a broad singlet at δ = 9.1 ppm. In the region between δ = 10.3 and 11.0 ppm the resonances of the NH^a and NH^b protons can be observed as broad singlets, which is a characteristic of Hamilton receptor derivatives. The pyrrolic NH^c protons of **1** resonate at δ ≈ –3 ppm.

Formation of the Supramolecular Depsipeptide Dendrimers 13–18

The assembly of the supramolecular depsipeptide dendrimers **13**–**18** was achieved by a fourfold complexation of **1** with depsipetide cyanurates **7**–**12**.[23] Each cyanurate **7**–**12** is bound to a complementary Hamilton receptor unit through six hydrogen bonds.

Effective binding of **1** with **7**–**12** can only be achieved in nonpolar aprotic solvents such as chloroform ($CHCl_3$) and CH_2Cl_2 (Scheme 2). However, **1** is insoluble in these solvents but it successively dissolves upon addition of **7**–**12**, forming the complexes **13**–**18**. The stepwise solubilisation can be monitored by the deepening of the colour of the solution as shown in Figure S1 (see Supporting Information).

The formation of **13**–**18** was demonstrated by UV/Vis, CD and NMR spectroscopy. Figure 2 shows the ^{1}H NMR spectra of the porphyrin derivative **1**, compound **7** and its corresponding complex **13** in the diagnostic δ = 4–11 ppm region. The alkyl chain protons 2-H resonate as a multiplet at δ = 4 ppm followed by five characteristic doublet signals of the benzyl protons 3-H and 9-H. The resonances of the protons 7-H and 8-H, which are located at the chiral centre of **7**, are two doublets at δ = 6 ppm. In the δ = 7–8 ppm region the spectrum shows the resonances of the aromatic protons, and at δ = 9 ppm the signal of the amide protons 1-H appears as a sharp singlet. After complexation with **1** the characteristic resonances and splitting patterns of the dendrimer protons barely change, with the exception of the signals of 1-H and 2-H. The alkyl protons 2-H in the complex **13** appear as a broad and slightly downfield-shifted (compared to the free dendron) multiplet. In addition to the resonances of the dendron protons 2-H to 15-H the ^{1}H NMR spectrum of the complex **13** shows a set of new signals, due to the Hamilton receptor substituted porphyrin **1**. In the downfield region the resonances of the NH^a and NH^b protons are observed as broad singlets at δ = 9.51 and 10.13 ppm. These chemical shifts are characteristic of



Scheme 2. General procedure for the synthesis of **13**–**18**: a) $CHCl_3$, room temperature, 16 h.

a Hamilton receptor containing a hydrogen-bonded cyanurate,[23] which clearly confirms the successful complexation. The signal patterns and the chemical shifts of the protons 16-H to 23-H within the complexes **13**–**18** are comparable to those in the free receptor **1**. In Figure 2c and in all ^{1}H NMR spectra of the compounds **13**–**18**, the signals of the amide protons 1-H of the dendrons are missing, which is the result of the dynamic character of the association of the complexes. As shown by temperature-dependent ^{1}H NMR experiments on complexes of **19** with **7**–**12**, the temperature range between 0–50 °C represents a coalescence regime.[23] This results in very broad and thus undetectable resonances of the amide 1-H protons of the bound and free depsipeptide cyanurates **7**–**12** at room temperature.[23] The pyrrolic NH^c protons of the complexes typically appear at $\delta \approx -3$ ppm as a broad singlet.

It has been reported before,[23,24] and has also been demonstrated in this study, that complexation through hydrogen bonding in similar systems results in pronounced downfield shifts of the resonances of the Hamilton receptor amide protons NH^a and NH^b. As a consequence, NMR titration experiments allow determination of the association constants. This is only possible, however, if all components are soluble in appropriate solvents such as chloroform or dichloromethane, so because of the insolubility of **1** in these solvents it was not possible to determine the association constants and binding cooperativitities of the 1:4 complexes **13**–**18** by NMR spectroscopy. On the other hand, NMR titration studies on 1:3 complexes of the homotritopic, chloroform-soluble Hamilton receptor **19** with the chiral depsipeptide dendrons **7**–**12** have been carried out successfully and can serve as a suitable model case for the complexation of **1** with the same dendrons.[23]

The clearly separated electronic absorptions of the porphyrin receptor **1** are well suited for the determination of chirality transfer, caused by the complexation of the chiral depsipeptide dendrons **7**–**12**, by CD spectroscopy. The UV/Vis spectrum of **1** (Figure 3a and d) is characterised by its two most intensive absorptions at λ_{max} = 300 and 420 nm, due to the bis(butyrylamino)pyridyl moieties (Hamilton re-

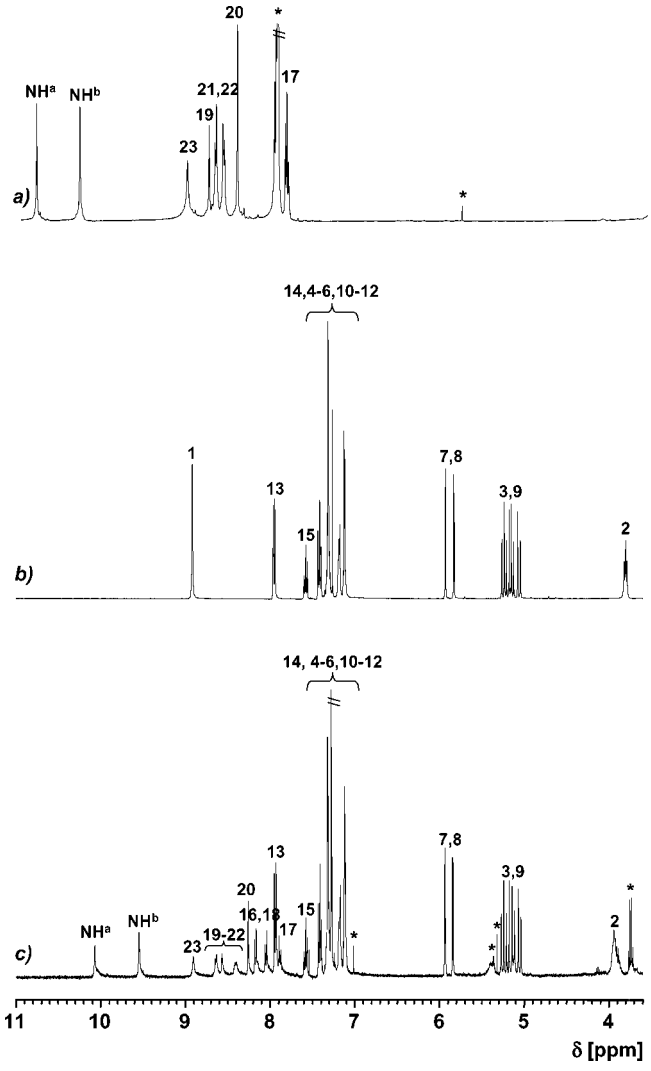
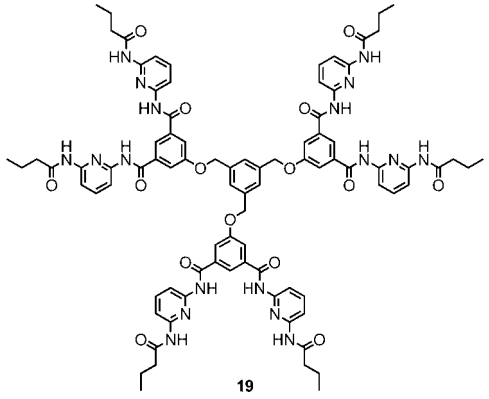


Figure 2. ^{1}H NMR spectra (δ = 3.6–11.0 ppm region, 400 MHz, room temperature): a) porphyrin derivative **1** ([D$_7$]DMF); b) depsipeptide dendron **7** ($CDCl_3$); c) its corresponding complex **13** ($CDCl_3$).



19

ceptor) and the Soret band of the porphyrin core, respectively. The relative intensities and the widths of these absorption bands strongly depend on the nature of the solvent: because of pronounced intermolecular hydrogen bonding in chloroform, in which **1** is almost insoluble, the Soret band is much broader and has a lower intensity than in THF (Figure 3d). In THF **1** is very soluble and no intermolecular hydrogen bonding takes place. The corresponding λ_{max} values, however, are independent of the solvent. The absorption spectra of the free dendrons **7**–**12** are characterised by the transitions of the aromatic units at 270 nm only (Figure 3b). The electronic absorption spectra of the complexes **13**–**18** each represent a superposition of those of the constituting components (Figure 3c) and are dominated by the absorptions of the porphyrin receptor **1**. Unlike in the case of the spectrum of the receptor **1** in chloroform, the Soret band is now the most intensive one: a consequence of the formation of the complexes **13**–**18**, accompanied by the disaggregation of **1** and the breaking of the intermolecular hydrogen bonds.

The CD spectra of the dendrons **7**–**12** are shown in Figure 4. Compounds **8**, **10** and **12** each display a positive Cotton effect in the area below 280 nm, while their corresponding enantiomers **7**, **9** and **11** each show perfect mirror image behaviour in the same region (Figure 4).[23] The intensities of the CD absorptions rise with the increasing generation number of the depsipeptide dendrons.

For the chiroptical investigation of the complexes **13**–**18**, 1 equiv. of the porphyrin receptor **1** was mixed with 4 equiv. of the corresponding depsipeptide-dendron **7**–**12** in HPLC-grade chloroform. Because of the insolubility of parent **1**, all solutions were stirred overnight in order to guarantee quantitative formation of the soluble complexes **13**–**18**. The first-generation complexes **13**–**14** showed no detectable Cotton effects in the region of the Hamilton receptor and porphyrin absorptions. This is due to very weak chirality transfer, attributed only to the two stereogenic centres in each depsipeptide dendron **7**–**8**. Even more importantly, the diastereoselective formation of a chiral superstructure can be ruled out. However, the CD spectra of the complexes **15**–**18**, involving the second- and third-generation dendrons **9**–**12**, revealed pronounced chirality transfer: two absorptions in the regions of the Hamilton receptor and the Soret band of the porphyrin at λ_{max} = 302 and 420 nm, respectively, were observed (Figures 5 and 6). Similarly to the absorption of the free dendrons (Figure 4) the CD spectra of **15**–**18** also display the Cotton effects of the chiral depsipeptide-dendrons **9**–**12** at λ_{max} = 260 nm. The spectra of the complexes of **15** and **17** show positive Cotton effects at 300 nm, together with negative Cotton effects in the Soret band region at 420 nm. On the other hand, complexes **16** and **18**, incorporating the corresponding enantiomeric dendrons of generation two and three, gave rise to CD spectra with opposite Cotton effects.

Significantly, the intensities of the CD absorptions in the regime of **1** at λ_{max} = 302 and 420 nm do not correlate with the generation number: the corresponding intensities of the second-generation systems **15** and **16** (Figure 5) are higher than those of the third-generation complexes **17** and **18** (Figure 6). This is especially true for the absorption at λ_{max} = 302 nm, caused by the chirality transfer to the Hamilton receptor unit of **1**. On the other hand, the optical activity in the dendron region at λ_{max} = 260 nm remains unaffected

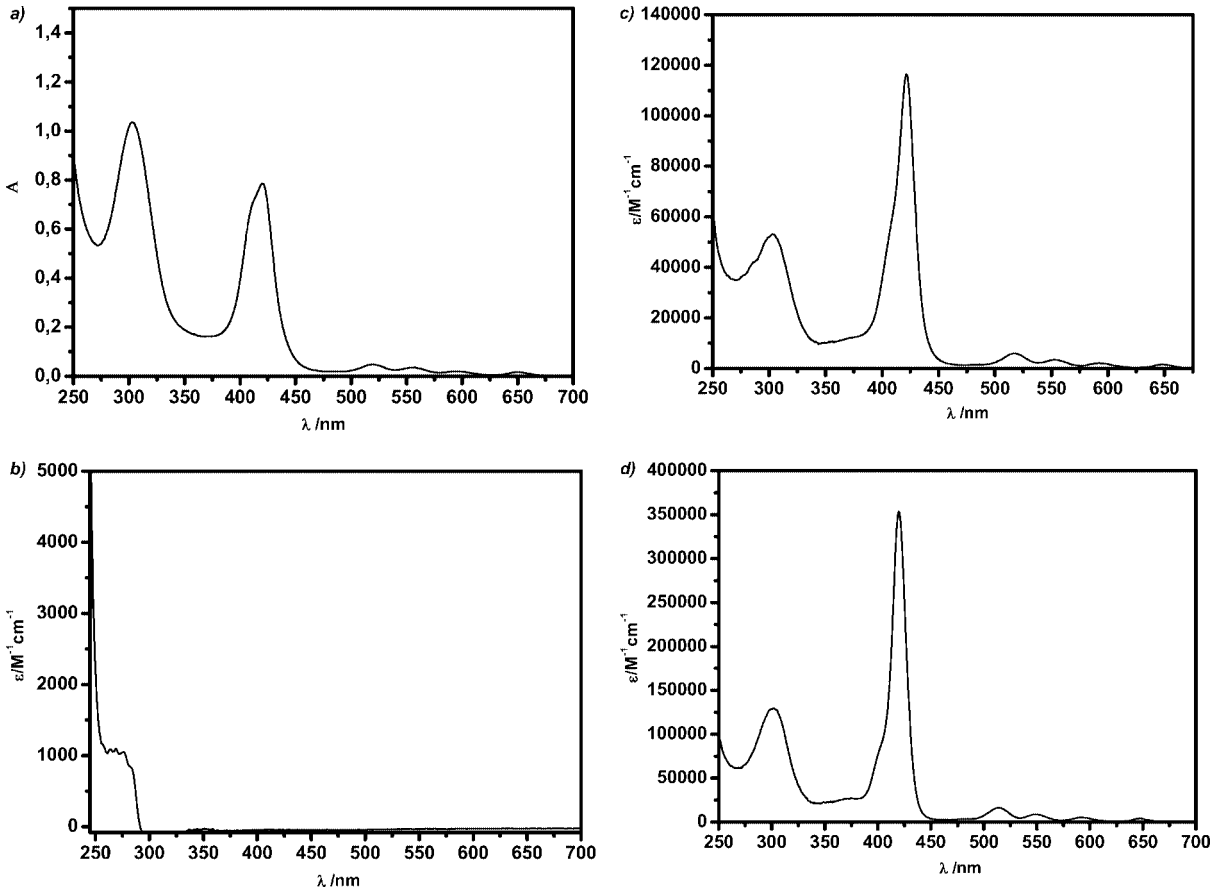


Figure 3. UV/Vis spectra: a) compound **1** in $CHCl_3$ (qualitative); b) compound **9** in $CHCl_3$; c) complex **13** in $CHCl_3$; d) compound **1** in THF.

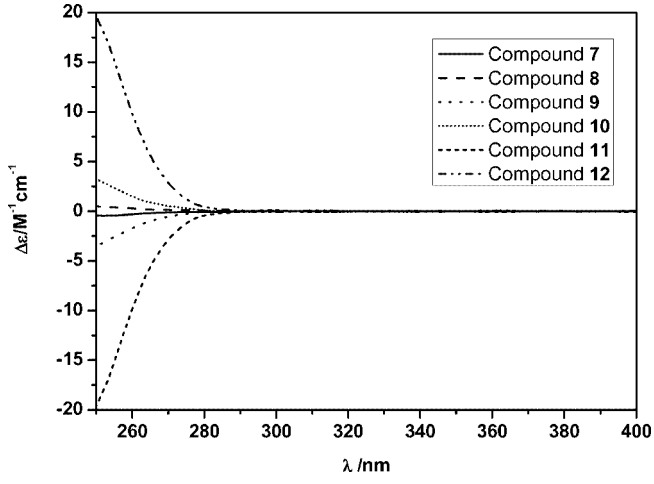


Figure 4. Circular dichroism (CD) spectra of the chiral depsipeptide dendrons **7**–**12** in $CHCl_3$ at 25 °C.

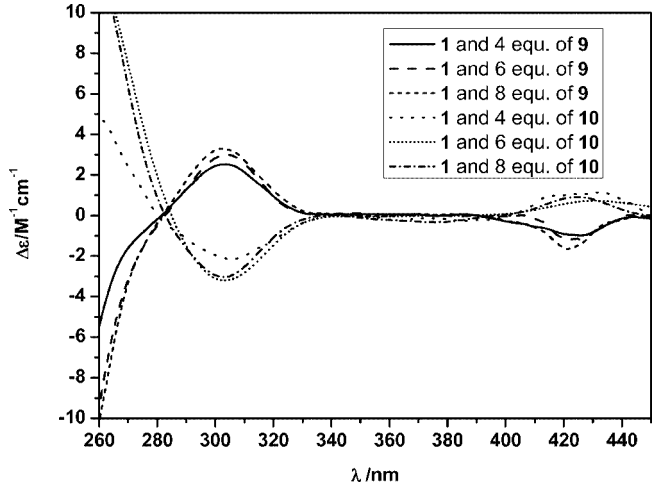


Figure 5. Circular dichroism (CD) spectra of the receptor **1** with 4–8 equiv. of the second-generation dendrons **9** and **10** in $CHCl_3$ at 25 °C.

and increases with the number of stereogenic centres in the same way as for the free dendrons **9**–**12** (Figure 5). The intensities of the CD absorptions at λ_{max} = 302 and 420 nm barely increase when excesses of the second- and third-generation dendrons **15**–**18** are used for the complexation with **1** (Figures 5 and 6). A possible explanation for this behaviour is the different steric requirements of the second- and third-generation dendrons **9/10** and **11/12**, respectively. As demonstrated for the complexation of these dendrons with the receptor **19**, containing three instead of four binding sites, the association constants and the positive cooperativity for threefold complexation are much more pronounced for the second-generation dendrons **9** and **10** than for the

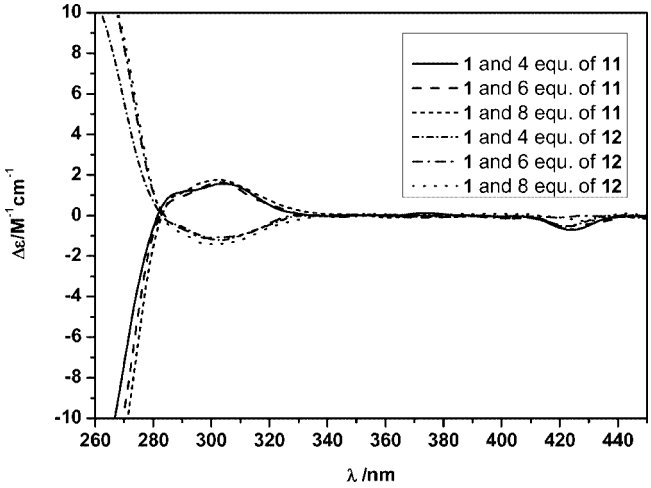


Figure 6. Circular dichroism (CD) spectra of the receptor **1** with 4–8 equiv. of the third-generation dendrons **11** and **12** in $CHCl_3$ at 25 °C.

third-generation dendrons **11** and **12**,[23] due to the fact that the third-generation systems are too bulky to allow an effective binding of the third dendron. As a consequence, only 50% of the core **19** is involved in a **19**:$\mathbf{L_3}$ complex (**L** = **11**, **12**) at a stoichiometric 1:3 ratio of **19** and **L**. Under the same conditions, on the other hand, about 90% of **19** is bound as **19**:$\mathbf{L_3}$ complex when the second-generation dendrons **9** and **10** are used. Although the benzene core of **19** is significantly smaller than the porphyrin core of **1**, the required fourfold binding may also cause overcrowding when the third-generation dendrons are allowed to react with **1** and the fraction of **1**:$\mathbf{L_4}$ (**L** = **11**, **12**) in a 1:4 mixture of the components can be considerably lower than 100%. If, on the other hand, the fourfold binding shows strong cooperativity, which is very likely to be the case in the complexation of the second-generation dendrons **9** and **10**, the **1**:$\mathbf{L_4}$ species can be considered predominant. It can be assumed that the most stable conformation of such a **1**:$\mathbf{L_4}$ complex should have a chiral propeller-like shape with two enantiomeric left-handed (Λ) or right-handed (Δ) conformations (Figure 7). X-ray crystal structures of a series of *meso*-aryl-substituted porphyrins showed that the aryl rings are in most cases not oriented perpendicularly to the porphyrin plane but exhibit typical angles in the range between 65 and 80°.[25] For this reason, the tetraphenylporphyrin moiety adopts chiral C_4-symmetrical conformations. This clearly demonstrates that such propeller-like conformations are preferred, which is also confirmed by quantum mechanical calculations (Figure 7).

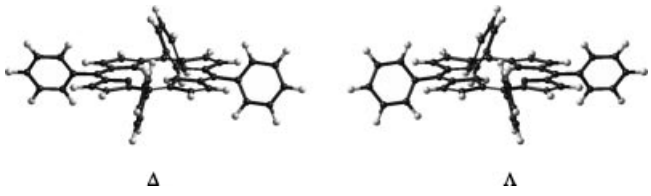


Figure 7. PM3-calculated[29] model of the C_4-symmetric propeller-shaped tetraphenylporphyrin with Δ and Λ configurations.

As the enantiomerically pure dendrons **9** and **10** with (all-*R*) and (all-*S*) configurations, respectively, were utilised, the formation of two diastereoisomers such as Λ-**1**:(all-*R*)-$\mathbf{10_4}$ and Δ-**1**:(all-*R*)-$\mathbf{10_4}$ is to be expected. One of these diastereomers will have a lower energy than the other and will be formed preferably. The presence of an excess of one diastereoisomer involving a chiral supramolecular motif will cause an increased intensity of the CD absorptions, which is actually observed in the complexes **15** and **16** in relation to the third-generation analogues **17** and **18**. Obviously, this phenomenon is much less pronounced for the complexation of the third-generation dendrons because the corresponding **1**:$\mathbf{L_4}$ complexes are less favoured and the diastereoselective formation of distinct chiral superstructures is less preferred. The scenario suggested here for the complexation of the second-generation dendrons **9** and **10** represents a case of supramolecular chirogenesis and has a variety of precedents: examples include chirality induction in achiral bis-[(octaethylporphyrin)zinc] (ZnD) by complexation of enantiomerically pure amino acids and other chiral amines and alcohols,[26] whilst related behaviour was also observed with a free-base porphyrin, covalently bound to eight peripheral (porphyrin)zinc units through enantiomerically pure nucleoside linkers[27] and a self-assembling system consisting of (porphyrin)zinc-appended foldamers and a chiral C_{60} adduct incorporating histidine moieties.[28] In the former case the optical activity of the nonaporphyrin system was interpreted in terms of the diastereoselective preference for a helical tetraphenylporphyrin conformation. A Cotton effect was observed in the Soret band region, resembling those of the complexes **15**–**18** (Figure 3), but much more pronounced. In the case of the supramolecular structure reported in ref.[28] the Cotton effect in the Soret band region is much less pronounced than those in **15**–**18**. Also in this case the preference for a specific helical conformation of the entire supramolecular construct involving phenylporphyrine building blocks was suggested.

Conclusions

In this work we present the synthesis of a new type of porphyrin-based tetrakis(Hamilton receptor) capable of forming chiral supramolecular dendrimers **13**–**18** with depsipeptide dendrons **7**–**12** incorporating cyanuric acid functionalities as their focal points. Chirality transfer from the depsipeptide dendrons to the porphyrin core was demonstrated by CD spectroscopy in the cases of the second- and third-generation complexes **15**–**18**. The intensities of the CD absorptions in the porphyrin region of the complexes are inversely proportional to the size of the dendrons, which points to a size-dependent cooperativity of the fourfold complexation of the dendrons, with more effective binding of the second-generation dendrons **9** and **10** than of their bulkier third-generation counterparts **11** and **12**. Pronounced cooperativity during the formation of the second-generation **1**:$\mathbf{L_4}$ complexes (**L** = **9**, **10**) is considered to be the reason for the diastereoselective formation of a pre-

ferred chiral conformation of the Hamilton receptor **1**, such as a propeller-like Λ or Δ conformation of the TPP unit in the complexes **15** and **16**. Such a scenario corresponds to a case of supramolecular chirogenesis.

Experimental Section

General Remarks: Commercially available chemicals were purchased from Aldrich, Fluka, Sigma and Acros Organics. 5,10,15,20-Tetrakis(*p*-carboxyphenyl)porphyrin (**6**) was purchased from Porphyrin Systems. Compound **2** and **3** were synthesised according to literature procedures.[24,25] The preparation of the chiral depsipeptide dendrimers **7**–**12** has been described previously.[23] Solvents were dried by standard techniques, dry DMF was obtained from Acros. HPLC-grade solvents were purchased from Acros Organics or SDS. Prior to use, HPLC-grade $CHCl_3$ was freshly distilled from potassium carbonate to avoid protonation of the free-base porphyrin **1**. Reactions were monitored by thin-layer chromatography (TLC) with Riedel–de Haën silica gel 60 F_{254} aluminium foils, detection by UV lamp. ^1H and ^{13}C NMR spectra were recorded with JEOL JNM EX 400, JEOL JNM GX 400 and JEOL A 500 instruments. The chemical shifts are given in ppm relative to tetramethylsilane (TMS) or the solvent peak as a standard reference. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet), unresolved signals as broad (br.) or very broad (v. br.). Mass spectra were measured with a Micromass Lab Spec (FAB) or a Finnigan MAT 900 spectrometer with 3-nitrobenzyl alcohol as a matrix. IR spectra were recorded with a React IR®-1000 ASI Applied Systems (ATR-DiComp-Detector) instrument on a diamond crystal. Analytical HPLC was performed with a Shimadzu LC-10 HPLC system (Nucleosil, 200×4 mm, particle size 5 μm, Macherey–Nagel), detection by photo diode array. Compound **1** was purified by preparative high pressure liquid chromatography with a Shimadzu LC-8A HPLC system (Nucleosil, 21×250 mm, particle size 5 μm, Macherey–Nagel), detection by UV/Vis. Circular dichroism (CD) measurements were carried out with a Jasco J 810 spectrometer with optical grade solvents and quartz glass cuvettes with a 2 mm path length. UV spectroscopy was performed with a Shimadzu UV-3102 spectrophotometer. Elementary analysis was carried out by combustion and gas chromatographic analysis with an EA 1110 CHNS analyzer (CE Instruments). Products were isolated by flash column chromatography (FC) (silica gel 60, particle size 0.04–0.063 nm, Merck).

Synthesis of Compound 4: Diacid **2** (7.49 g, 15.69 mmol) was suspended in $SOCl_2$ (149 mL), and dry DMF (1 mL) was added under N_2. The suspension was heated at reflux, and after 2 h the solid had entirely dissolved and the reaction mixture was heated at reflux for a further 3 h. The excess of $SOCl_2$ was distilled off and the oily residue was kept under high vacuum for 60 min. The crude dichloride was used without further purification. A solution of the dichloride in dry THF (60 mL) was added dropwise at room temp. to a solution of **3** (6.19 g, 34.54 mmol) and triethylamine (3.51 g, 34.54 mmol) in dry THF (60 mL). The reaction mixture was stirred at room temp. for 30 min and heated at reflux for another 12 h. After cooling to room temp., the solution was filtered, concentrated to dryness, and purified by flash column chromatography (SiO_2; EtOAc/hexane, 60:40; R_f = 0.46). Yield 3.2 g (34%), slightly yellow solid, m.p. 169 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.93 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH_3), 1.70 (m, 4 H, CH_2), 2.30 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 7.38 (m, 2 H, Py), 7.50 (m, 2 H, Bz), 7.58 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, Bz), 7.71 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Py), 7.83 (s, 4 H, Bz, Bn), 8.00 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, Py), 8.10 (s, 1 H, Bn), 8.55 (br., 2 H, CONH), 8.66 (br., 2 H, CONH) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 13.7 (CH_3), 18.7, 39.3 (CH_2), 109.7, 110.3 (Py), 122.9, 125.0 (Bn), 128.1, 128.7, 130.3, 134.3 (Bz), 135.9 (Bn), 140.7, 148.9, 150.0 (Py), 151.3 (Bn), 163.7, 165.2, 172.1, (C=O) ppm. React-IR (thin film): $\tilde{\nu}_{max}$ = 3243, 2954, 2937, 1743, 1689, 1586, 1530, 1454, 1321, 1285, 1103, 1095, 1046, 1023, 980, 854, 782, 730 cm^{-1}. MS (FAB): *m*/*z* = 609 $[M]^+$. $C_{33}H_{32}N_6O_6$ (608.7): calcd. C 65.12, H 5.30, N 13.81; found C 64.80, H 5.42, N 13.67.

Synthesis of Compound 5: A solution of KOH (1.84 g, 32.8 mmol) in water (200 mL) was added dropwise at room temp. to a solution of **4** (1.00 g, 1.64 mmol) in dioxane (400 mL). The reaction was allowed to proceed for 48 h and the dioxane was evaporated. The pH of the remaining solution was adjusted to 2 by the addition of concentrated HCl and the solvents were evaporated to dryness. The residue was suspended in water (25 mL) and filtered. The filter residue was washed with water (80 mL) and cold EtOAc (10 mL) and dried under reduced pressure. Yield: 500 mg (61%) of a brownish-yellow solid, m.p. 154 °C (decomposition). ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.94 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH_3), 1.64 (m, 4 H, CH_2), 2.42 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 7.62 (s, 2 H, Bn), 7.70 (m, 2 H, Py), 7.96 (d, $^3J_{H,H}$ = 5.1 Hz, 4 H, Py), 8.09 (d, $^4J_{H,H}$ = 1.0 Hz, 1 H, Bn), 10.55 (br., 2 H, CONH), 10.97 (br., 2 H, CONH) ppm. ^{13}C NMR (100.5 MHz, [D$_6$]DMSO, 25 °C): δ = 13.5 (CH_3), 18.2, 38.0 (CH_2), 109.9, 110.3 (Py), 118.4 (Bn), 118.8 (Py), 135.5, 141.9 (Bn), 149.4, 149.8 (Py), 158.3 (Bn), 166.2, 173.4 (C=O) ppm. React-IR (thin film): $\tilde{\nu}_{max}$ = 2968, 1652, 1586, 1532, 1444, 1324, 1293, 1243, 1216, 1154, 1000, 876, 799, 710, 668 cm^{-1}. MS (FAB, NBA): *m*/*z* = 1009 [2 M]$^+$, 505 $[M]^+$. $C_{26}H_{28}N_6O_5 \times 1.5\,H_2O$ (532.24): calcd. C 60.57, H 6.06, N 16.30; found C 60.94, H 5.69, N 16.07.

Synthesis of Compound 1: EDC (407 mg, 2.13 mmol) and DMAP (260 mg, 2.13 mmol) were added at room temp. to a solution of compound **5** (957 mg, 1.88 mmol) and 5,10,15,20-tetrakis(*p*-carboxyphenyl)porphyrin (**6**) (300 mg, 0.38 mmol) in dry DMF (8 mL). The reaction was allowed to proceed for 7 d in the dark and the crude reaction product was precipitated with water. The precipitate was collected by filtration, washed with water (3×20 mL) and air-dried overnight. The reaction product was dried under reduced pressure at 50 °C for 1 d and purified by repeated column chromatography (SiO_2; THF, THF/CH_2Cl_2, 80:20; R_f = 0.95) followed by preparative HPLC (Nucleosil; THF/CH_2Cl_2, 80:20). Yield: 52 mg (5%), purple solid, m.p. 300 °C (decomposition). ^1H NMR (400 MHz, [D$_7$]DMF, 25 °C): δ = –2.69 (br., 2 H, NH), 0.96 (t, $^3J_{H,H}$ = 7.3 Hz, 24 H, CH_3), 2.74 (m, 16 H, CH_2), 2.78 (t, $^3J_{H,H}$ = 7.4 Hz, 16 H, CH_2), 7.94 (m, 8 H, Py), 8.02 (m, 16 H, Py), 8.50 (d, $^4J_{H,H}$ = 0.8 Hz, 8 H, Bn), 8.67 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, Bn), 8.77 (d, $^3J_{H,H}$ = 8.3 Hz, 8 H, Bn), 8.84 (s, 8 H, Bn), 9.11 (s, 8 H, pyrrole β-H), 10.39 (br., 8 H, CONH), 10.92 (br., 8 H, CONH) ppm. ^{13}C NMR (100.5 MHz, [D$_7$]DMF, 25 °C): δ = 13.93 (CH_3), 19.4, 39.1 (CH_2), 110.4 (Py), 120.2 (Bn), 125.8 (Py), 126.1, 129.5, 135.8, 137.2, 140.7, 151.5 (Bn), 152.0 (Py), 163.0, 165.7, 173.0 (C=O) ppm. React-IR (thin film): $\tilde{\nu}_{max}$ = 1671, 1584, 1293, 1241, 1177, 1067, 797, 729 cm^{-1}. UV/Vis (THF): λ_{max} (ε) = 301 (142000), 420 (429000), 515 (19600), 547 (9320), 590 (6150) nm. MS (FAB): *m*/*z* = 2736 $[M]^+$.

Complexation of 1 with 7: Dendron **7** (4 equiv., 1.49 mg, $22.52 \cdot 10^{-4}$ mmol) was added to compound **1** (1.54 mg, $5.63 \cdot 10^{-4}$ mmol), suspended in $CHCl_3$ (5 mL, HPLC grade). The solution was stirred at room temp. for 13 h. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.81 (br., 2 H, pyrrrole NH), 0.83–2.43 (m, 88

H, CH_2, CH_3), 3.90 (m, 8 H, CH_2N), 5.00 (d, $^2J_{H,H}$ = 12.1 Hz, 4 H, Bn-CH_2), 5.07 (d, $^2J_{H,H}$ = 12.1 Hz, 4 H, Bn-CH_2), 5.14 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, Bn-CH_2), 5.20 (d, $^2J_{H,H}$ = 12.1 Hz, 4 H, Bn-CH_2), 5.80 (d, $^3J_{H,H}$ = 2.81 Hz, 4 H, CH*), 5.89 (d, $^3J_{H,H}$ = 2.81 Hz, 4 H, CH*), 7.07–7.39 (m, 48 H, Bn, Bz), 7.49 (m, 4 H, Bz), 7.85 (t, $^3J_{H,H}$ = 8.1 Hz, 8 H, Py), 7.87 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, Bz), 8.02 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, Py), 8.14 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, Py), 8.21 (s, 8 H, Bn) 8.37 (br., 8 H, Bn), 8.54 (br., 8 H, Bn), 8. 61 (s, 4 H, Bn-CH), 8.87 (br., 8 H, pyrrole β-H), 9.51 (br., 8 H, CONH), 10.03 (br., 8 H, CONH) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 302 (98000), 421.5 (142000), 518.5 (7000), 552.5 (4000), 591.5 (2000), 647.5 (2000) nm.

Complexation of 1 with 8: Dendron **8** (4 equiv., 1.49 mg, $22.52 \cdot 10^{-4}$ mmol) was added to compound **1** (1.54 mg, $5.63 \cdot 10^{-4}$ mmol), suspended in $CHCl_3$ (5 mL, HPLC grade). The solution was stirred at room temp. for 13 h. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.81 (br., 2 H, pyrrole NH), 0.83–2.43 (m, 88 H, CH_3, CH_2), 3.93 (m, 8 H, CH_2N), 5.09 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, Bn-CH_2), 5.16 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, Bn-CH_2), 5.22 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, Bn-CH_2), 5.28 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, Bn-CH_2), 5.80 (d, $^3J_{H,H}$ = 2.81 Hz, 4 H, CH*), 5.88 (d, $^3J_{H,H}$ = 2.81 Hz, 4 H, CH*), 7.06–7.44 (m, 48 H, Bn, Bz), 7.51 (m, 4 H, Bz), 7.84 (t, $^3J_{H,H}$ = 7.9 Hz, 8 H, Py), 7.9 (d, $^3J_{H,H}$ = 7.9 Hz, 8 H, Bz), 8.11 (d, ^3J (H,H) = 8.2 Hz, 8 H, Py), 8.13 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, Py), 8.21 (s, 8 H, Bn), 8.32 (br., 8 H, Bn), 8.52 (br., 8 H, Bn), 8.56 (br., 4 H, Bn), 8.83 (br., 8 H, pyrrole β-H) 9.48 (br., 8 H, CONH), 9.99 (br., 8 H, CONH) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 302 (98000), 422 (142000), 519 (7000), 552 (4000), 592.5 (2000), 649 (2000) nm.

Complexation of 1 with 9: Dendron **9** (4 equiv., 3.47 mg, $22.52 \cdot 10^{-4}$ mmol) was added to compound **1** (1.54 mg, $5.63 \cdot 10^{-4}$ mmol), suspended in $CHCl_3$ (5 mL, HPLC grade). The solution was stirred at room temp. for 13 h. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.88 (br., 2 H, pyrrole NH), 0.84–2.42 (m, 152 H, CH_3, CH_2), 3.15 (m, 24 H, CH_2N), 3.84 (br., 4 H, CONH), 5.01 (d, $^2J_{H,H}$ = 3.1 Hz, 4 H, Bn-CH_2), 5.03 (d, $^2J_{H,H}$ = 3.1 Hz, 4 H, Bn-CH_2), 5.09 (d, 4 H, Bn-CH_2), 5.10 (d, 4 H, Bn-CH_2), 5.16 (d, $^2J_{H,H}$ = 1.9 Hz, 4 H, Bn-CH_2), 5.19 (d, $^2J_{H,H}$ = 2.7 Hz, 8 H, Bn-CH_2), 5.22 (d, $^2J_{H,H}$ = 2.8 Hz, 4 H, Bn-CH_2), 5.69 (d, $^3J_{H,H}$ = 3.7 Hz, 4 H, CH*) 5.77 (d, $^3J_{H,H}$ = 2.8 Hz, 8 H, CH*), 5.79 (d, $^3J_{H,H}$ = 2.8 Hz, 4 H, CH*), 5.88 (d, $^3J_{H,H}$ = 2.9 Hz, 4 H, CH*), 5.90 (d, $^3J_{H,H}$ = 2.8 Hz, 4 H, CH*), 7.06–7.56 (116 H, Bn, Bz), 7.89 (t, 8 H, Py), 7.97 (m,16 H, Bz), 8.00 (m, 24 H, Bz, Py-CH), 8.12 (d, $^3J_{H,H}$ = 7.9 Hz, 8 H, Py-CH), 8.21(s, 8 H, Bn-CH), 8.34 (br., 8 H, Bn-CH), 8.52 (br., 12 H, Bn-CH), 8.85 (br., 8 H, pyrrole β-H), 9.48 (br., 8 H, CONH), 10.02 (br., 8 H, CONH) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 303 (53000), 421.5 (117000), 517.5 (6000), 552.5 (3000), 592 (2000), 648 (2000) nm.

Complexation of 1 with 10: Dendron **10** (4 equiv., 3.47 mg, $22.52 \cdot 10^{-4}$ mmol) was added to compound **1** (1.54 mg, $5.63 \cdot 10^{-4}$ mmol), suspended in $CHCl_3$ (5 mL, HPLC grade). The solution was stirred at room temp. for 13 h. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.88 (br., 2 H, pyrrole NH), 0.85–2.42 (m, 152 H, CH_2, CH_3), 3.18 (m, 24 H, CH_2N), 3.84 (br., 4 H, CONH), 5.01 (d, $^2J_{H,H}$ = 4.5 Hz, 4 H, Bn-CH_2), 5.05 (d, $^2J_{H,H}$ = 4.5 Hz, 4 H, Bn-CH_2), 5.09 (d, $^2J_{H,H}$ = 3.0 Hz, 4 H, Bn-CH_2), 5.12 (d, $^2J_{H,H}$ = 2.4 Hz, 4 H, Bn-CH_2), 5.16 (d, $^2J_{H,H}$ = 3.1 Hz, 4 H, Bn-CH_2), 5.20 (d, $^2J_{H,H}$ = 3.8 Hz, 8 H, Bn-CH_2), 5.23 (d, $^2J_{H,H}$ = 3.8 Hz, 4 H, Bn-CH_2), 5.69 (d, $^3J_{H,H}$ = 3.7 Hz, 4 H, CH*), 5.78 (d, $^3J_{H,H}$ = 2.8 Hz, 8 H, CH*), 5.81 (d, $^3J_{H,H}$ = 2.8 Hz, 4 H, CH*), 5.89 (d, $^3J_{H,H}$ = 2.8 Hz, 4 H, CH*), 5.92 (d, $^3J_{H,H}$ = 2.8 Hz, 4 H, CH*), 6.22 (br., 4 H, CONH), 7.10–7.53 (116 H, Bn, Bz), 7.90 (t, 8 H, Py), 7.92 (m, 16 H, Bz), 8.00(m, 24 H, Bz, Py), 8.11 (d, $^3J_{H,H}$ = 8.0 Hz, 8 H, Py) 8.21 (s, 8 H, Bn), 8.24, (br., 8 H, Bn), 8.65 (br., 8 H, Bn), 8.81 (s, 4 H, Bn), 8.87 (br., 8 H, pyrrole β-H), 9.48 (br., 8 H, CONH), 10.02 (br., 8 H, CONH) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 302 (53000), 422 (117000), 518 (6000), 552 (3000), 592 (2000), 648 (2000) nm.

Complexation of 1 with 11: Dendron **11** (4 equiv., 7.42 mg, $22.52 \cdot 10^{-4}$ mmol) was added to compound **1** (1.54 mg, $5.63 \cdot 10^{-4}$ mmol), suspended in $CHCl_3$ (5 mL, HPLC grade). The solution was stirred at room temp. for 13 h. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.82 (br., 2 H, pyrrole NH), 0.83–2.45 (m, 280 H, CH_2, CH_3), 3.18 (m, 56 H, CH_2N), 3.84 (br., 16 H, CONH), 5.18 (m, 64 H, Bn-CH_2), 5.87 (m, 56 H, CH*), 6.62 (br., 8 H, CONH), 7.07–8.01 (m, 324 H, Bn, Bz, Py), 8.10 (d, 8 H, Py), 8.21 (s, 8 H, Bn), 8.32 (br., 8 H, Bn), 8.54 (br., 12 H, Bn), 8.84 (br., 8 H, pyrrole β-H), 9.50 (br., 8 H, CONH), 9.96 (br., 8 H, CONH) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 277.5 (55000), 284 (55000), 302 (53000), 421.5 (109000), 517 (6000), 553 (3000), 592 (2000), 648 (1000) nm.

Complexation of 1 with 12: Dendron **12** (4 equiv., 7.42 mg, $22.52 \cdot 10^{-4}$ mmol) was added to compound **1** (1.54 mg, $5.63 \cdot 10^{-4}$ mmol), suspended in $CHCl_3$ (5 mL, HPLC grade). The solution was stirred at room temp. for 13 h. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.83 (v. br., 2 H, pyrrole NH), 0.84–2.46 (m, 280 H, CH_2, CH_3), 3.15 (m, 56 H, CH_2N), 5.17 (m, 64 H, Bn-CH_2), 5.84 (m, 56 H, CH*), 6.60 (br., 8 H, CONH), 7.06–8.02 (m, 324 H, Bn, Bz; Py), 8.09 (d, 8 H, Py), 8.21 (s, 8 H, Bn), 8.25 (br. 8 H, Bn), 8.53 (m, 12 H, Bn), 8.83 (br., 8 H, pyrrole β-H), 9.44 (br., 8 H, CONH), 9.95 (br., 8 H, CONH) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 276.5 (55000), 284.5 (55000), 302.5 (53000), 422 (109000), 517 (6000), 552.5 (3000), 592 (2000), 648.5 (1000) nm.

Supporting Information (see footnote on the first page of this article): Solubilisation studies concerning the stepwise formation of complex **18**.

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