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Synthesis and chiroptical properties of a new type of chiral depsipeptide dendrons

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Abstract—A new type of chiral depsipeptide dendrons based on tartaric acid as branching juncture and ω-aminocapronic acid as spacer has been prepared. Natural and unnatural tartaric acid building blocks have been incorporated, providing access to combinatorial libraries. All compounds have been completely characterized by FAB-MS, EA analysis, $^{1}H/^{13}C$ NMR- and UV/Vis-spectroscopy. ^{1}H NMR relaxation measurements have been used to examine the conformational flexibility of these dendrons in CH_3CN and CH_3OH and indicate a less flexible structure in CH_3CN. Pulse gradient spin echo (PGSE) NMR measurements correlate these findings to molecular dimensions. A reduced size for the dendrons in CH_3CN compared to CH_3OH leads to the assumption of a more compact structure in this solvent. Additional polarimetric data reveal, that observed changes in optical activity with increasing generation can in CH_3OH be explained by constitutional effects of the dendron structure but not in CH_3CN. CD measurements are in agreement with these findings and show a linear increase of the Cotton effects with increasing generation for CH_3OH but not for CH_3CN. It can be concluded that the conformation within the dendrons is very sensitive to environmental conditions and that a chiral secondary structure might be stabilized in CH_3CN. Initial studies revealed that chirality transfer to the focal functionality occurs.

1. Introduction

Chirality is a characteristic property of biopolymers such as proteins and DNA in nature and is crucial in the interplay between structure and function.[1] Originating from small chiral monomers it is often expressed in an asymmetric superstructure, for example, a helix. Noncovalent interactions result in a folding process that produces distinctive three-dimensional environments.[2] Only the correctly assembled globular structure enables the macromolecules to fulfill their various functions e.g. chiral recognition, enantioselective catalysis, clathration and transport of small molecules. An important goal in mimicking biology is therefore to delineate the factors which govern macromolecular asymmetry. Dendrimers[3] can be considered as model compounds for natural macromolecules because of their well-defined, highly ordered and globular structure. Furthermore, incorporating chiral units should open the possibility to study the effect of chirality in macromolecular systems.[4,5] Chiral dendrimers bear the potential to build up a more or less rigid asymmetric shape with a chiral surface and chiral cavities. The expression of chirality in the form of a secondary conformational order would then be observable by chiroptical methods.[6] In the studies reported so far the presence of a secondary structure could be unambiguously ascertained in a system by Parquette.[7] It is described how intramolecular hydrogen-bonding, solvophobic compression and non-covalent packing interactions result in a helical conformation. However, most systems consisting of chiral branching units could not assign for certain a secondary structure or suggest a lack of conformational order.[8]

Recently, we introduced the concept of chiral depsipeptide dendrimers.[8h] This new class of dendrimers closely resembles the structure of natural depsipeptides which consist of α-hydroxy and α-amino acids, connected by ester and amide linkages.[9] As branching units, tartaric acid derivatives were chosen, and as spacer, various di- and tripeptides were attached. In the synthetic sequence, C-protected amino acids or peptides were coupled by amide formation reactions to tartaric acid derivatives with one unprotected carboxylic group. The synthesis of higher generation dendrimers was carried out by a repetitive C-deprotection of the peptides and a subsequent coupling with the deprotected hydroxy groups of the tartaric acid derivatives. However, because of the complex synthesis and demanding purification processes only small amounts of third generation dendrimers could be made accessible.[8h] Therefore the deduction of the chiroptical properties of the dendrons and their use as peptide mimetic building blocks in synthesis was limited.

Now we report on a different concept for the synthesis of depsipeptide dendrons based on tartaric acid as branching juncture and ω-aminocapronic acid as spacer. Compared to

Keywords: depsipeptide dendrimers; dendrimer conformation; solvent dependant folding; pulse gradient spin echo (PGSE) measurements; circular dichroism.

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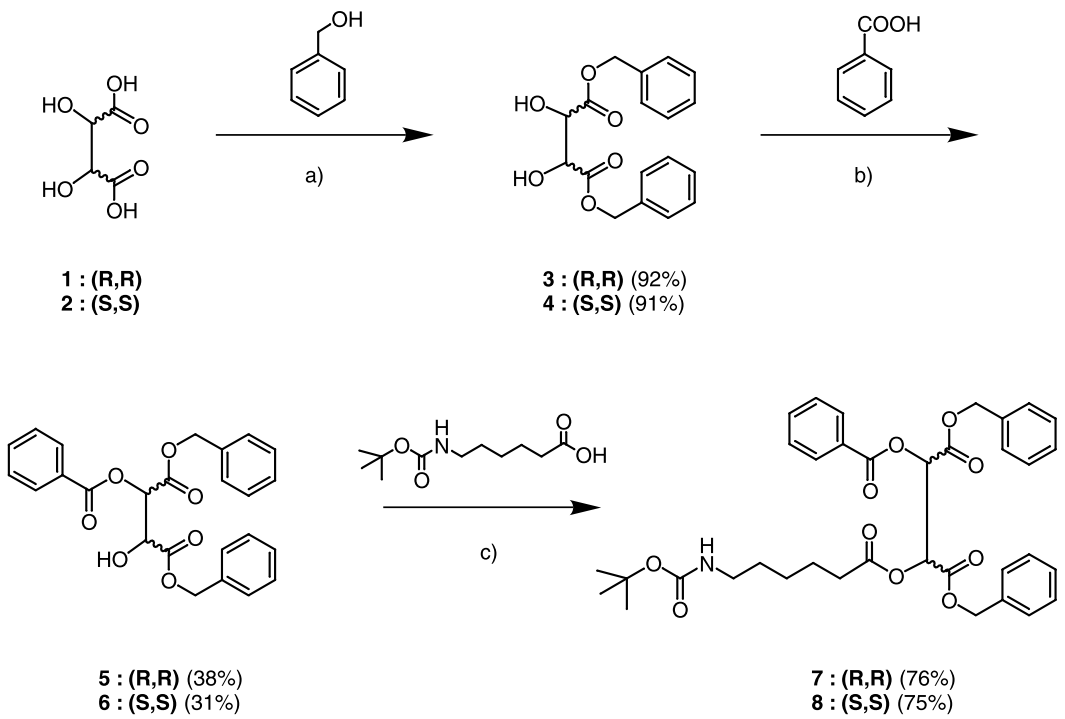


Scheme 1. (a) pTSA, 107°C, benzene; (b) DMAP, HOBt, DCC, CH_2Cl_2; (c) DCC, HOBt, CH_2Cl_2.

the previous concept the overall synthetic sequence could be shortened by circumventing the multi-step synthesis of the peptide spacer. Furthermore the reactivity of the branching juncture was reversed and now the repetitive units are connected by amide instead of ester bond formation, which results in higher yields for the coupling steps. Most of the chiral dendrimers reported so far consist of only one enantiomeric form of the chiral building blocks. Here we incorporated both the natural and unnatural tartaric acid, providing access to libraries of various enantiomers and diastereomers. The chiroptical properties are reported in regard to solvent conditions. Furthermore, in an initial attempt, the use of the dendrons as chiral micro-environments is demonstrated by attaching anthracene chromophores to the focal functionality.

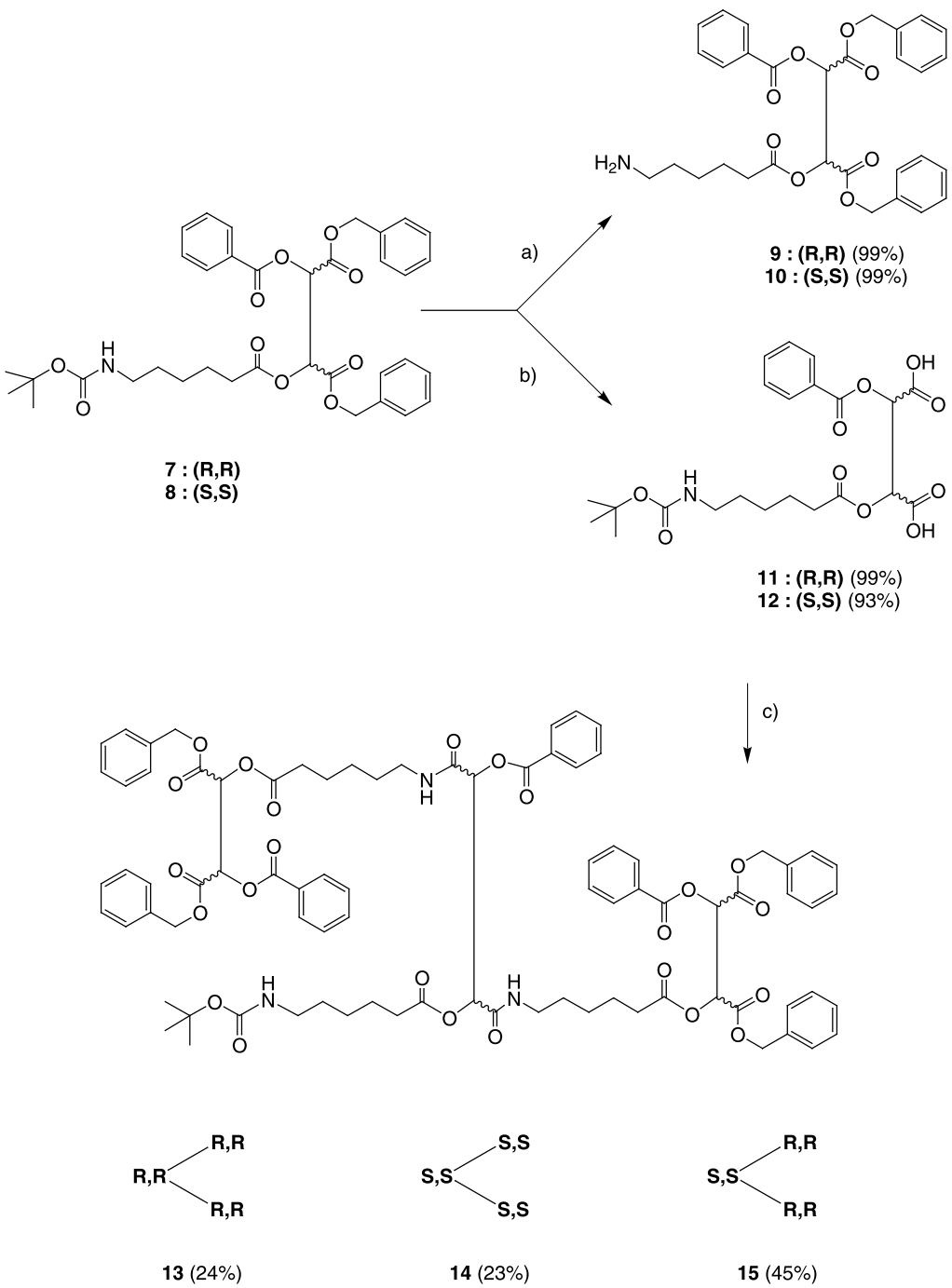
2. Results and discussion

2.1. Synthesis of the depsipeptide dendrons

The synthesis of the key building blocks is depicted in Scheme 1. First generation dendrons **7** and **8** were synthesized using a Steglich coupling[10] of tartaric acid derivatives **5** and **6**, and BOC-protected ω-aminocapronic acid. To prevent the rearrangement of activated ω-BOC-aminocapronic acid[10] the use of HOBt was essential. Considering that it is an early step in dendron synthesis, the yields of 70–75% are satisfactory. A simple purification method allowed the facile preparation of **7** and **8** on a 30 g scale. The tartaric acid derivatives **5** and **6** were obtained by protecting the carboxylic groups of natural and unnatural tartaric acid **1** and **2** with benzylic alcohol in 92% yield, followed by protection of one hydroxy group of **3** and **4** by benzoic acid in a statistical reaction (38% yield). Altogether, the yield of the first generation dendrons **7** and **8** was ~27% based on the tartaric acids **1** and **2**, respectively. Furthermore, in all these steps no chromatographic separation process was necessary.

For the growth of the dendritic branches the amino functions of **7** and **8** were deprotected with trifluoroacetic acid (Scheme 2).[11] After the removal of the solvent, **9** and **10** were obtained as TFA adducts in 99% yield. Deprotection of the carboxylic groups was carried out by stirring **7** and **8** with 10% Pd/C in MeOH in an H_2-atmosphere for 24 h. After filtration of the catalyst and removal of the solvent, **11** and **12** were obtained in 99% yield. No further purification was required. Reaction of the diacids **11** and **12** with the amines **9** and **10** under typical peptide coupling conditions (DCC, HOBt, 0°C)[11] afforded the enantiomers **13**, **14** and the diastereomer **15** in 25 and 45% yield, respectively (Scheme 2). Note that the outer shell of **15** is similar to **13** but the inner layer is enantiomeric to **14**.

Repetition of this reaction cycle, including deprotection of **13**, **14**, **15** and coupling with **11** or **12** gave third generation dendrons **19**, **20** and **21** (Scheme 3). The same reaction conditions led to a yield of 16% for the enantiomeric compounds **19** and **20**, and to 71% yield for the diastereomer **21** in all attempts. The different yields are surprising if it is considered that the configurational difference for example between **15** and **13** is located at a distance of 9 atoms and 10 bonds. However, a similar observation was made by Seebach.[12] Here the effect was even more pronounced, since in their synthetic sequence some diastereomers would not form at all. A further coupling after deprotection of these dendrons did not occur. Instead, only the corresponding fourth generation monoamides have been isolated. Thus, for the successful



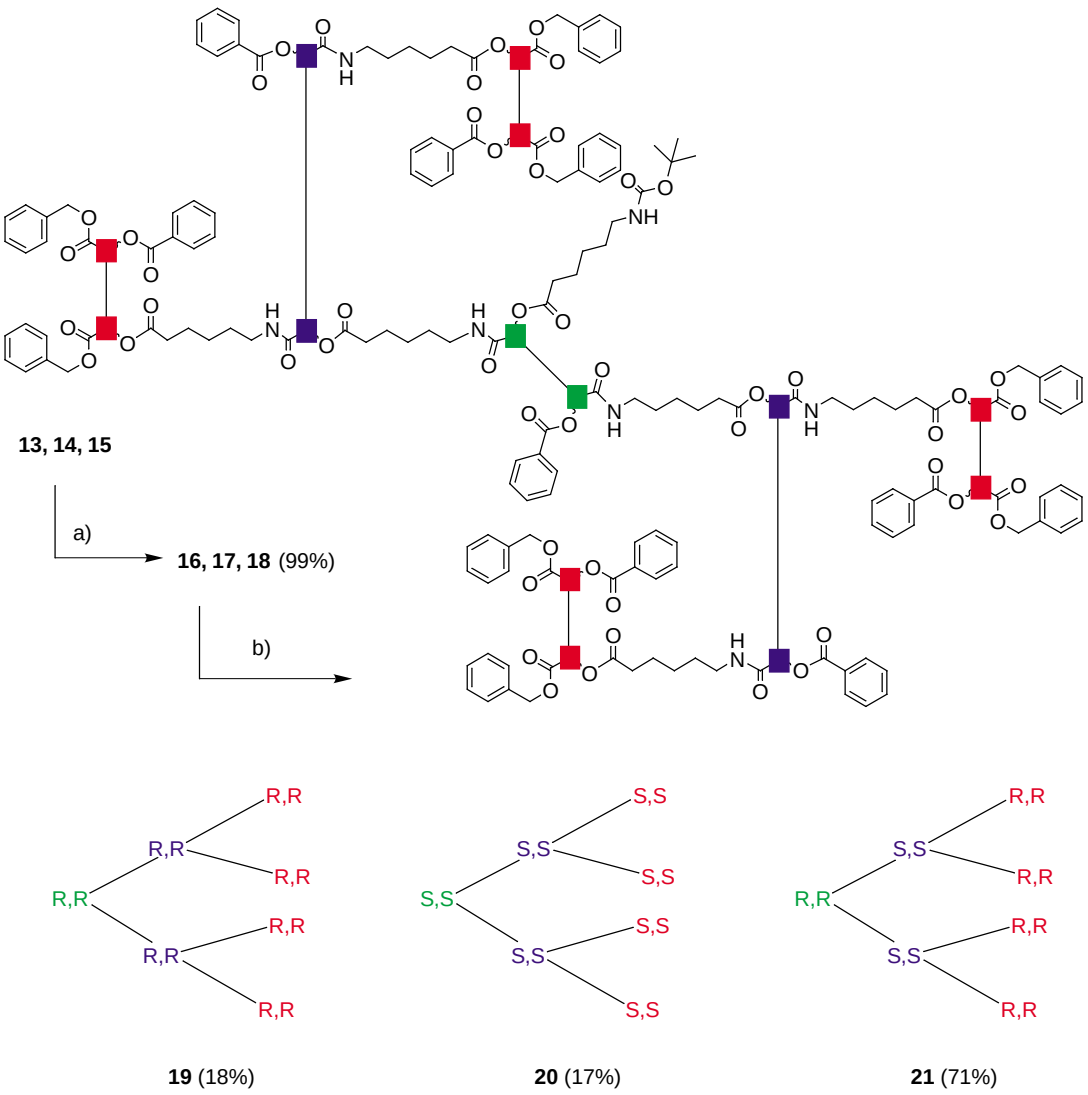
Scheme 2. (a) TFA, CH_2Cl_2; (b) H_2, Pd/C, CH_3OH; (c) DCC, HOBt, NEt_3, CH_2Cl_2.

preparation of higher generation branches an elongation of the diacids **11** and **12** might be necessary to reduce steric congestion.

All dendrons were isolated as colorless solids. They are highly soluble in unpolar and polar aprotic solvents such as CH_2Cl_2, CH_3CN and toluene and they are readily soluble in polar protic solvents such as CH_3OH, EtOH. The R_f values of the second generation dendrons **13**–**15** (EtAc/hex 1:1; silica gel) did not show large differences (**13**, **14** R_f=0.33; **15** R_f=0.34). However, in the third generation dendrons the differences between the diastereomers **19**–**21** become remarkable (**19**, **20** R_f=0.15, **21** R_f=0.08; CH_2Cl_2/MeOH 25:1; silica gel).

2.2. Characterization

All dendrons were characterized by ^1H and ^{13}C NMR, UV, mass spectrometry, elemental analysis, and by their specific and molar optical rotations $[\alpha]_D$ and $[\phi]_D$. FAB mass spectroscopy confirmed the expected molecular weights and revealed the purity of the samples. Typically, the base peak corresponds to $[M-BOC]^+$, whereas $[M+H]^+$ is small but noticeable.



Scheme 3. (a) TFA, CH_2Cl_2; (b) **11**, **12**, DCC, HOBt, NEt_3, CH_2Cl_2.

2.2.1. $^1H/^{13}C$ NMR spectroscopy. A characteristic feature of these chiral systems is that all C- and H- atoms are topologically different even if they originate from identical layers in the dendron. This is reflected by the splitting of the signals throughout all NMR-spectra. In the ^1H NMR spectra of the third generation dendron **20** (recorded in CD_3CN, Fig. 1C) the signals of the aromatic protons are located in the range between δ=7.0–8.3, while the signals of the alkyl and BOC protons are located between δ=1.0–3.4. The singlet of the *t*-butyl protons of the BOC-group appears at δ=1.38. The alkyl protons next to the ester group linkages resonate at δ=2.2 as well resolved multiplets, whereas the protons in close vicinity to the amide groups lead to broad multiplets at δ=3.16. Characteristic are the regions between δ=5.0–5.4 and δ=5.5–6.0, where the resonances of the peripheral benzylic C*H*$_2$-groups and the C*H*-protons of the tartaric acid units are localized (Fig. 1C). Two different sets of N–*H* signals are found. The signal at δ=5.35 is attributed to the amide proton of the BOC-group and the set of signals at δ=6.9 is assigned to the remaining N–*H* protons. In the aromatic region the *ortho* protons of the benzyloxy groups experience strong deshielding and are located at δ=7.8 and δ=8.1. The gradual change of the dendritic microenvironment on going from outside to inside along the three layers leads to a gradual downfield shift of the ^1H nuclei. The protons of the different layers of the tartaric acid units were assigned by integration and give rise to distinct sets of signals over a broad range of ~0.5 ppm (Fig. 1C and Scheme 3, first layer depicted in green, second layer depicted in blue, third layer depicted in red). The same is true for the protons in close vicinity to the amid groups (~0.1 ppm) (δ=3.10–3.20). Even more pronounced is the effect for the *ortho* nuclei of the aromatic benzyloxy groups (~0.1–0.25 ppm) (δ=7.8–8.1). The corresponding shifts of other ^1H nuclei which are located in the interior of the dendron could not be determined exactly due to close signal overlapping. Similar observations are reported by Seebach[13] in $^1H/^{19}F$ NMR spectra and by ^1H NMR studies of Stoddart[14] and Meijer.[15] No significant differences in chemical shifts between the pairs of enantiomers and the corresponding diastereomer throughout all generations have been observed for the same groups of ^1H-nuclei. Furthermore, no line broadening was observed in CD_3CN for all stereoisomers up to second generation and for **19**

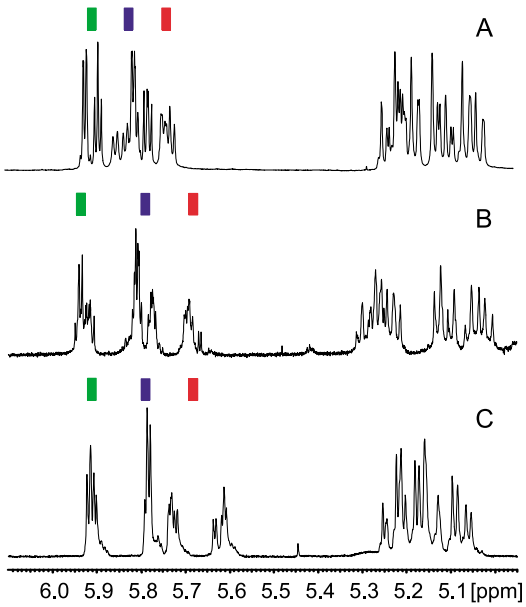


Figure 1. ^{1}H NMR spectra of **20** in $CDCl_3$ (**A**), CD_3OD (**B**) and CD_3CN (**C**) at room temperature (section of the C*H*-protons of the tartaric acid building blocks). first layer depicted in green, second layer depicted in blue, third layer depicted in red.

and **20** even up to third generation. However, a small line broadening effect was detectable for third generation dendron **21**.

To study the interaction of these dendrons with the solvent and the effects of the solvent on the conformation of the dendrons we recorded ^{1}H NMR spectra in DMSO-d_6, $CDCl_3$, CD_3CN and CD_3OD. Even though the characteristic regions of the resonances remain roughly unchanged, the signal splitting differs significantly (Fig. 1). However, based only on these investigations it cannot be decided whether this is due to a normal solvent shift or due to an adaption of different conformations. As a consequence we carried out detailed NMR investigations.

2.2.2. T_1 relaxation times. To study the segmental mobility of the distinct layers in the dendron with regard to the solvent, we determined the spin-lattice relaxation times (T_1) of the tartaric acid units in the aprotic and protic solvents

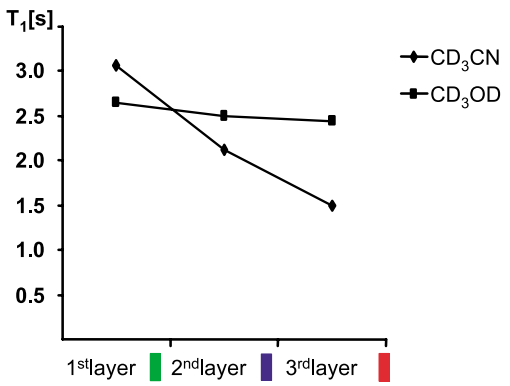


Figure 2. Dependence of T_1 of the C*H*-protons of the tartaric acid building blocks on the position in dendron **20**.

CD_3CN and CD_3OD, respectively. The measurements were performed using the standard inversion-recovery method.[16] In Figure 2 the T_1 relaxation times are plotted as a function of the position of the tartaric acid units in the dendron. For CD_3OD the relaxation times remain independent of the position of the unit throughout the whole dendron, whereas in CD_3CN the relaxation times decrease by going to the outer layer. Therefore the segmental mobility decreases in CD_3CN on going to the periphery.[17] To the contrary, the segmental mobility is independent of the position of the unit in the dendron in CD_3OD. Referring to the conformations in solution, it can therefore be assumed, that the structure of the dendron is less flexible in CD_3CN, with the various layers influencing each other. In CD_3OD the conformational flexibility is more pronounced.

2.2.3. PGSE NMR Experiments. Pulsed-field gradient nuclear magnetic resonance (PGSE) provides a powerful tool for measuring translational motion in solution. The method relates the attenuation of the echo signal from a Hahn spin-echo pulse sequence containing a magnetic field gradient pulse in each τ period to the adjournment of the observed spins and therefore the related molecules. The signal intensities are hence connected to diffusion rates and allow the resolution of molecular extensions.[18] In our case, PGSE NMR is used to further analyse conformational ordering within the dendrons. If the conformation of the dendrons is more compressed and folded in CD_3CN compared to CD_3OD this should be clearly seen in the observed molecular dimensions. Diffusion coefficients are experimentally determined by observing the decay of the signal intensity as a function of increasing gradient strength. The decrease depends on the diffusion rates of the spin-labelled molecules. For sine gradient pulses the following Stejskal–Tanner equation is applied:[18b]

$$E_{\sin} = \exp\left(-\gamma^2 g^2 D\delta^2\left[\cos^2\left(\frac{N\pi}{2}\right)3\delta + \sin^2\left(\frac{N\pi}{2}\right)(4\Delta - \delta)\right]/(N\pi)^2\right) \quad (1)$$

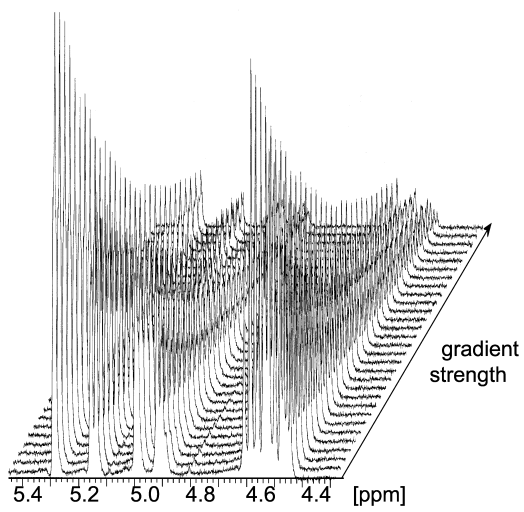


Figure 3. Stacked plot ^{1}H NMR spectra of dendron **20** in DMSO-d_6 acquired with increasing gradient strength at 298 K.

Table 1. Diffusion coefficients and hydrodynamic radii R_H of dendron **20** in different solvents determined by ^{1}H-PGSE NMR measurements

Solvent	D (m^2/s)	R_H (nm)	d (nm)
CD_3OD	2.60×10^{-10}	1.54	3.08
DMSO-d_6	7.30×10^{-11}	1.55	3.10
CD_3CN	4.87×10^{-10}	1.29	2.58

where γ is the gyromagnetic ratio, δ is the duration of the gradient pulse, Δ is the delay between the gradient pulses, D is the diffusion coefficient, g is the gradient strength and $2N$ denotes the period of the gradient pulse. The self diffusion coefficients were now determined from the slope of ln (I/I_o) versus g^2.

Figure 3 shows a 2D NMR spectrum of **20** in DMSO-d_6. The decay of the signal intensity is displayed in relation of chemical shift to gradient strength. However, the behaviour of **20** in CD_3OD compared to **20** in CD_3CN is quite different. The decay is considerably slower, which is based on a smaller diffusion coefficient and therefore on a larger molecular size. The Stokes–Einstein equation was used to determine the hydrodynamic radii R_H from the obtained diffusion coefficients:

$$R_H = \frac{k_B T}{6\pi\eta D} \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the solvent. The results are combined in Table 1. The dependence of the dendron size on the solvent is evident. Whereas in the protic solvent CD_3OD an average diameter of 3 nm was determined, the aprotic polar solvent CD_3CN causes a more compressed size of 2.6 nm. In DMSO the average diameter is 3 nm.

Based on the results of the NMR experiments we conclude, that depending on the solvent, different conformations evolve in the third generation dendrons, as demonstrated with the example of **20**. We assume that in CD_3OD it adopts an (open) structure which allows free interaction of the solvent molecules with the interior functionalities. In CD_3CN a more compact structure is developed leading to a reduced size and to restricted segmental mobilities.[19]

2.2.4. Optical rotation measurements. The chiroptical properties of all dendrons have been investigated in order to determine the significance of the chiral repeating units on the structure of the whole dendron. The optical activity of the chiral dendrons have been normalized to the number of chiral repeating units and compared to the optical activity of first generation dendrons **7** and **8**, respectively. Deviations from the estimated values indicate the establishment of preferred chiral conformations of the dendrons.[8] Specific ($[\alpha]_D$) and molar rotations ($[\phi]_D$) of the dendrons **7**, **8**, **13**–**15** and **19**–**21** were recorded in CH_3OH (Table 2) and in CH_3CN (Table 3). In an initial comparison of the molar rotation per chiral subunit as a function of generation we observed for the dendrons **13**–**21** a decrease with increasing dendron generation (Fig. 4). The $[\phi]_D/n$-values (n number of chiral repeating units) for second generation dendrons **13** and **14** are 35% (CH_3OH) smaller than that for first shell

Table 2. Chiroptical data for dendrons **7**–**23** in MeOH

Compound	Observed $[\alpha]_D$[a]	Observed $[\phi]_D$[b]	Concentration[c]	Estimated $[\phi]_D$[d]/deviation[e] (%)
8	−61	−394	0.202	–
14	−50	−760	0.184	−738 (3)
20	−44	−1431	0.204	−1426 (<1)
15	+61	+925	0.202	+840 (9)
21	+54	+1785	0.218	+1631 (9)
7	+61	+395	0.210	–
22	+6	+50	0.123	–
23	−6	−49	0.122	–

[a] Specific rotation (10^{-1} deg cm^2 g^{-1}).
[b] Molar rotation (10 deg cm^2 mol^{-1}).
[c] Concentration (g 100 ml^{-1}).
[d] Molar rotation (10 deg cm^2 mol^{-1}).
[e] In brackets.

Table 3. Chiroptical data for dendrons **7**–**23** in CH_3CN

Compound	Observed $[\alpha]_D$[a]	Observed $[\phi]_D$[b]	Concentration[c]	Estimated $[\phi]_D$[d]/deviation[e] (%)
8	−40	−262	0.215	–
14	−25	−389	0.212	−471 (17)
20	−21	−715	0.130	−889 (20)
15	+42	+655	0.194	+575 (14)
21	+39	+1273	0.188	+1096 (16)
7	+40	+261	0.218	–
22	+6	+53	0.102	–
23	−6	−54	0.104	–

[a] Specific rotation (10^{-1} deg cm^2 g^{-1}).
[b] Molar rotation (10 deg cm^2 mol^{-1}).
[c] Concentration (g 100 ml^{-1}).
[d] Molar rotation (10 deg cm^2 mol^{-1}).
[e] In brackets.

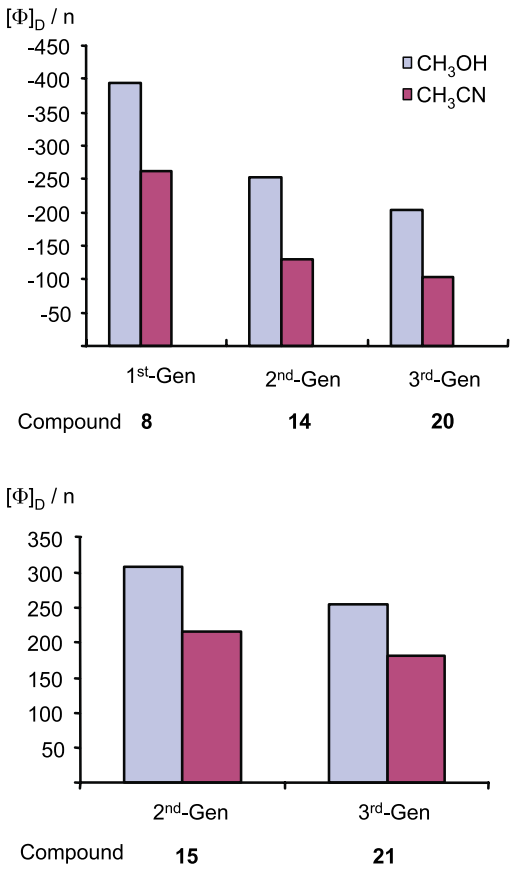
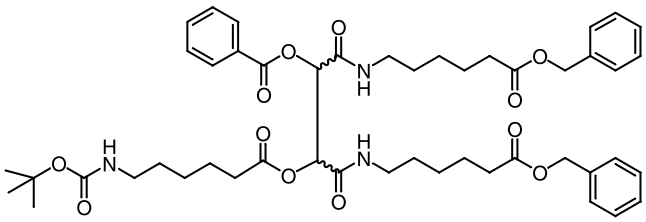


Figure 4. Molar optical rotations [Φ] per tartaric acid building block (first generation) for dendrons **8**, **14**, **15**, **20** and **21** in CH_3OH and CH_3CN.

dendrons **7** and **8**. For third generation dendrons **19** and **20** the $[\phi]_D/n$-values (from first to third generation) deviate by 48% (CH_3OH). In CH_3CN the deviation is 51% (**13**, **14**) (from first to second generation) and 61% (**19**, **20**) (from first to third generation), respectively. For the mixed dendrons **15** and **21** we found a positive overall $[\phi]_D/n$, resulting in a disagreement of 58% (**15**) (from first to second generation) and of 34% (**21**) (from first to third generation) in CH_3OH. In CH_3CN the deviation is 60% (**15**) (from first to second generation) and 42% (**21**) (from first to third generation). However, the question is whether **7** and **8** are suitable model compounds to rule out constitutional effects resulting from different positions of the chiral units within the dendron. The importance of suitable model compounds was emphasized by McGrath et al.[8a,b] Thus, we chose **22** and **23** as model compounds for the first and second layers. The only difference compared to the dendrons **7** and **8** is the peripheral benzyl ester moiety. The polarimetry data show, that this deviation distal to the asymmetric C-atoms does greatly effect the optical activity. The replacement of the benzylesters by an amide bonded alkyl group results in a change in sign of the $[\phi]_D$-value.[20] In CH_3OH the $[\phi]_D$-value of natural tartaric acid (*R*,*R*) derivative **22** is slightly negative (-49), while the $[\phi]_D$-value of first generation dendron **7** (*R*,*R*) is positive (+395) (Table 2). In CH_3CN the same is true (**7**; $[\phi]_D$=+261) and **22**; $[\phi]_D$=−54). The subunits within the periphery of the second and third generation dendrons **13**–**15** and **19** –**21** have identical constitutions and resemble the first shell dendrons **7** and **8**, respectively. Therefore no appropriate model compound is needed. Based on **7**, **8**, **22** and **23** as model units the agreement between the estimated and observed $[\phi]_D$-values of the homologue dendrons **13**, **14**, **19** and **20** is now in the range of 3% in MeOH (Table 2). Dendrons **15** and **21** consisting of a mixture of natural and unnatural tartaric acid building blocks deviate by ~9%. This close match between the estimated and the observed values leads to the conclusion that no additional chiral folding of the entire dendrons **13**, **14**, **19** and **20** in CH_3OH is involved. Therefore the changes observed with increasing dendron generation can be interpreted to be based solely on constitutional changes in the dendron structure and are not caused by a conformational ordering.[8a] The reason of the deviation of the diastereomeric dendrons **15** and **20** from the estimated $[\phi]_D$ -values remains unclear. Interestingly, when the optical activity is calculated from the corresponding $[\phi]_D$-values of the constituting units obtained in CH_3CN the values disagree significantly more, on average by 18% for all dendrons (Table 3). In fact the disagreement in aprotic CH_3CN relative to a close fit in CH_3OH might suggest that intramolecular communication of the chiral subunits in CH_3CN (but not in CH_3OH) results in a fragile stabilization of chiral conformations.



22 : R, R
23 : S, S

2.2.5. Circular dichroism measurements. To gain further information about the chiroptical properties of the depsipeptide dendrons, circular dichroism (CD) spectra were recorded in CH_3OH (Fig. 5) and CH_3CN (Fig. 6).[21] As a measure of chirality the electronic $\pi-\pi^*$ transition of the benzene chromophores at 237 nm can be used. As

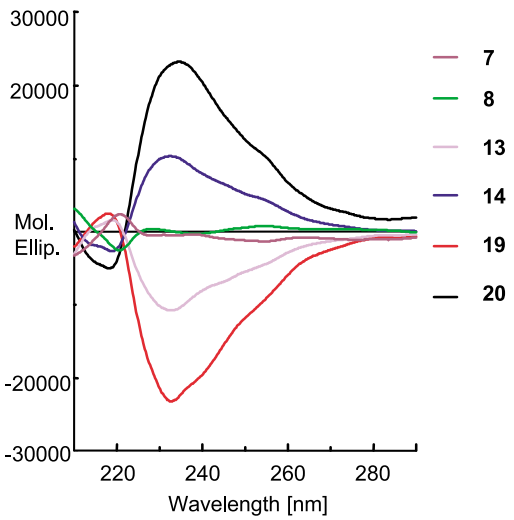


Figure 5. CD spectra of **7**, **8**, **13**, **14**, **19** and **20** in CH_3OH. (Mol. Ellip. in [10 deg cm^2 mol^{-1}]).

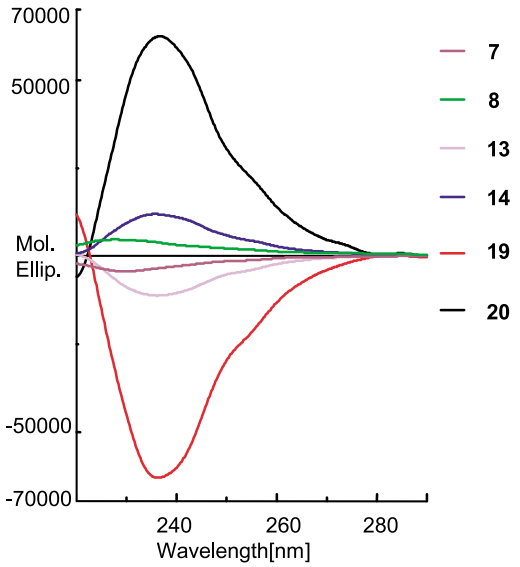


Figure 6. CD spectra of **7**, **8**, **13**, **14**, **19** and **20** in CH_3CN. (Mol. Ellip. in [10 deg cm^2 mol^{-1}]).

determined from UV-spectra of compounds **7**, **8**, **22** and **23** the molar absorptivity (ε) is roughly proportional to the number of benzene chromophores in all solvents. The maximum in the absorption spectra at 237 nm coincides with a maximum in the CD spectra. However, first generation dendrons **7** and **8** exhibit intra-chromophoric excitonic coupling at 237 nm. On the contrary, with increasing generation number the dendrons cannot adopt prevailing conformations suitable for exciton coupling.[22] In CH_3OH the second and third generation dendrons **14** and **20** display a positive Cotton effect at 237 nm and a negative Cotton effect at 215 nm. The enantiomeric compounds **13** and **19** behave vice versa. In CH_3CN the spectra do not change shape significantly and the Cotton effects do not shift. For dendrons **15** and **21**, which consist of natural and unnatural tartaric acid building blocks, the situation is slightly different (Fig. 7). Both display positive Cotton

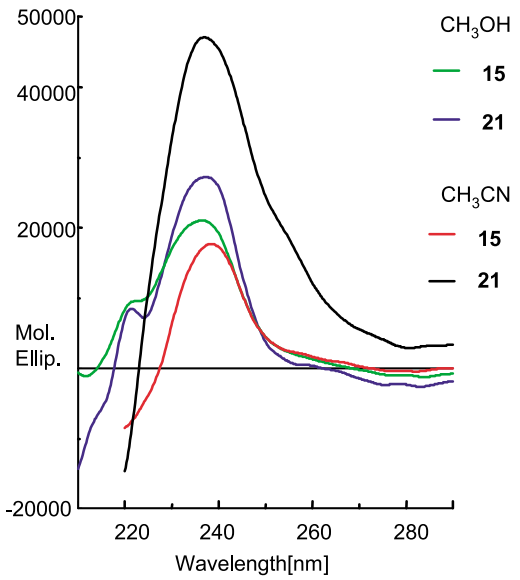


Figure 7. CD spectra of **15** and **21** in CH_3OH and CH_3CN. (Mol. Ellip. in [10 deg cm^2 mol^{-1}]).

effects at 247 nm and at 215 nm in CH_3OH. In CH_3CN a significant change in the spectra occurs and the latter Cotton effect disappears. It is interesting to note the evaluation of the magnitudes of the Cotton effects in these solvents. In CH_3OH the Cotton effects of the dendrons **13**–**15** and **19**–**21** are nearly proportional to the number of chromophores present and the molar extinction coefficents increase linearly with the generation number. By changing to the aprotic solvent CH_3CN this linear relationship was lost. Whereas second generation dendrons **13** and **14** are roughly in line, the increase in absorption going to the third generation dendrons **19** and **20** is significantly enlarged (Fig. 6) and is not proportional to the number of chromophores present anymore. Even more pronounced is this behavior in the spectra of the diastereomers **15** and **21** (Fig. 7). In CH_3CN the third generation dendron **21** exhibits a smaller Cotton effect than second generation dendron **15**. Whereas the CD-spectra measured in CH_3OH do not provide any indication about the formation of a chiral superstructures the use of CH_3CN as solvent for CD-investigations suggests the possibility of stabilization of chiral secondary structures.

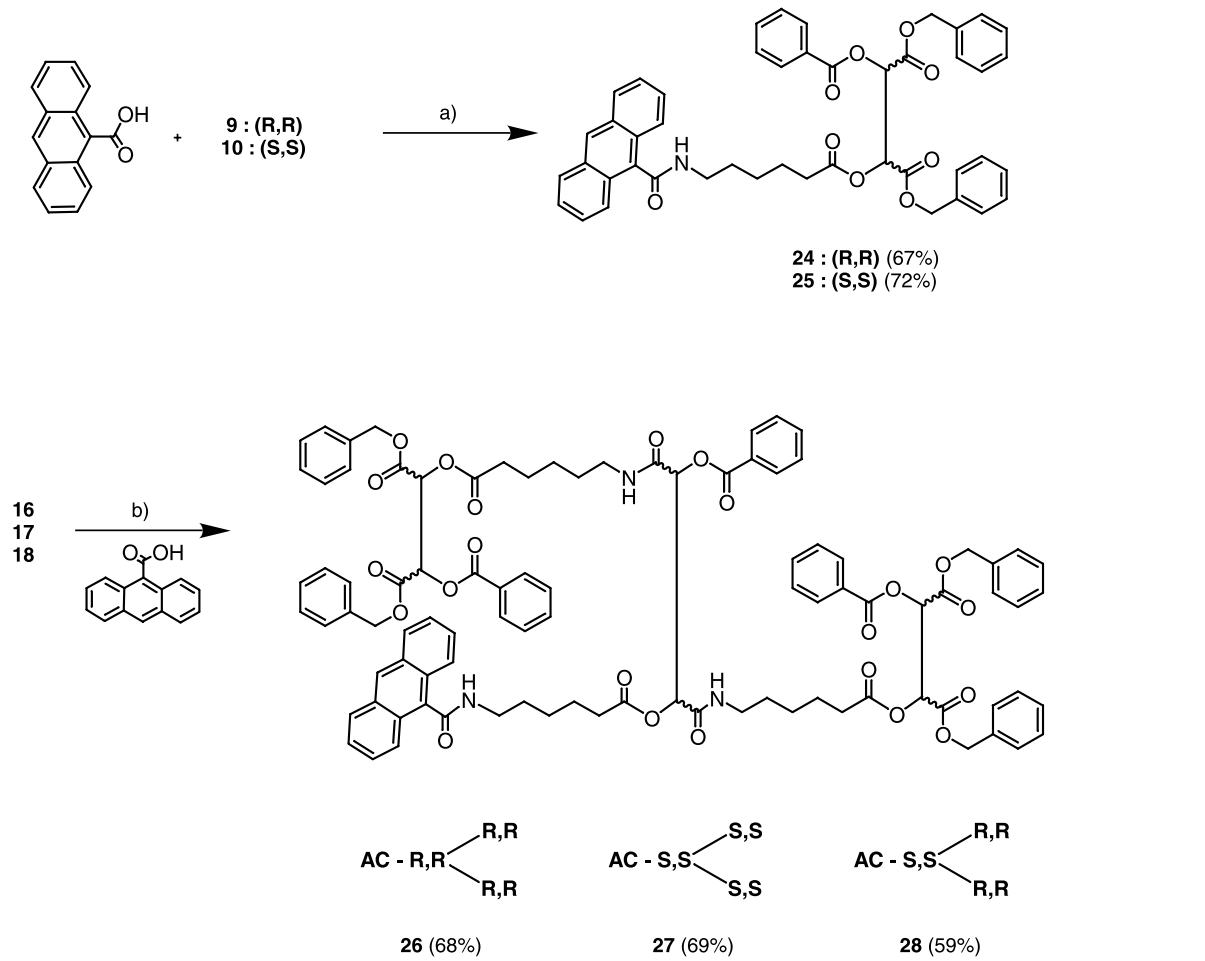
These results are in agreement with the NMR measurements and the polarimetric data described above. It might be assumed that the conformation of the dendrons in solution is very sensitive to the conditions used. However, based on the present data it cannot be decided whether this would be single stable conformers or an equilibrium between several forms including achiral folding motifs which is probably the more likely situation.

2.3. Chirality transfer

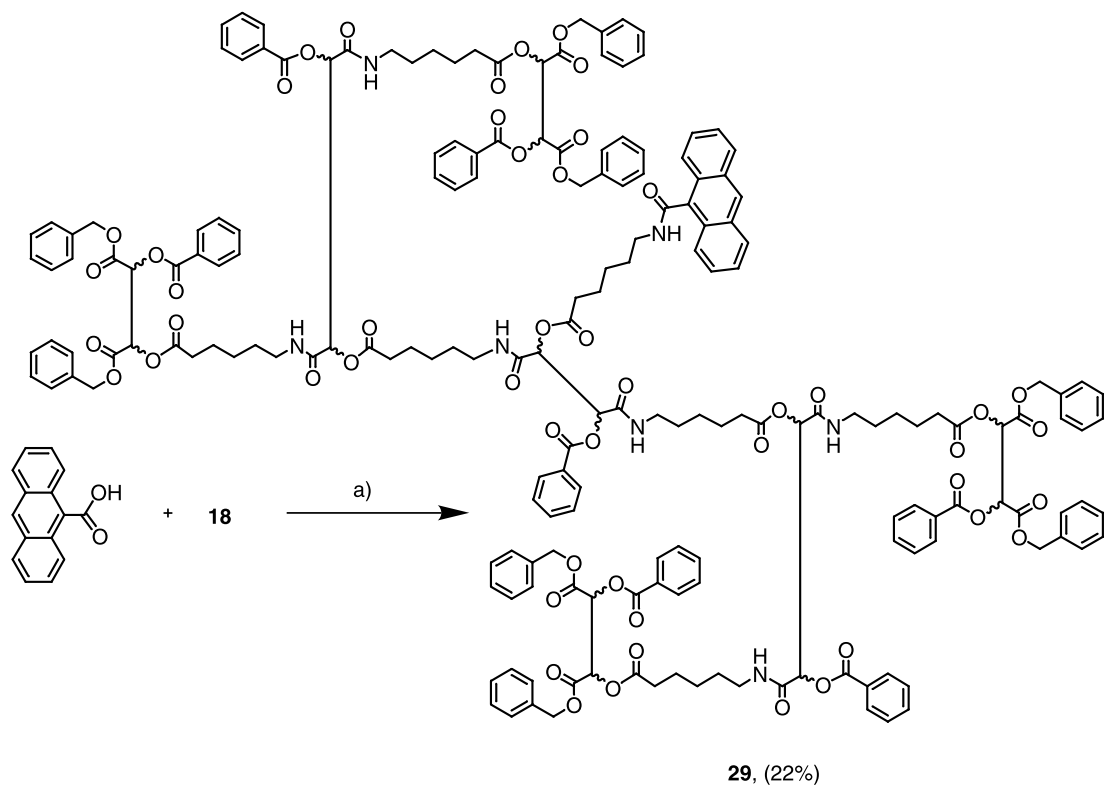
The ability to transmit chiral information over comparatively large distances represents an important factor in applications such as catalysis and molecular recognition, which are envisaged for dendritic macromolecules.[23] Therefore we were interested if the chiral information embodied in our dendrons could be transferred to the focal point. In an initial concept the focal amino-functionalities of the dendrons were connected to 9-anthracene carboxylic acid (Schemes 4 and 5). The synthesis was straightforward and conditions normally used for peptide coupling were applied.[11] To test whether the chiral information was transferred we recorded CD-spectra in CH_3OH in the region of the absorption of the anthracene chromophore. In fact a new cotton effect appeared at the absorptionn of the anthracene chromophore (254 nm) (Fig. 8). As a preliminary result we can conclude, that the microenvironment around the focal group is distinctively chiral. In a further examination we will test if there is an amplification of chirality under modified conditions (e.g. temperature and solvent).

3. Summary and conclusions

We have prepared a new series of chiral depsipeptide dendrons consisting of natural and unnatural tartaric acid building blocks as branching units and ω-aminocapronic acid as spacer. These monodisperse systems reaching molecular weights up to 3284 amu were completely characterized by FAB-MS, $^1H/^{13}C$ NMR- and UV/Vis-spectroscopy.



Scheme 4. (a) DCC, HOBt, NEt_3, CH_2Cl_2; (b) DCC, HOBt, NEt_3, CH_2Cl_2.



Scheme 5. (a) DCC, HOBt, NEt_3, CH_2Cl_2.

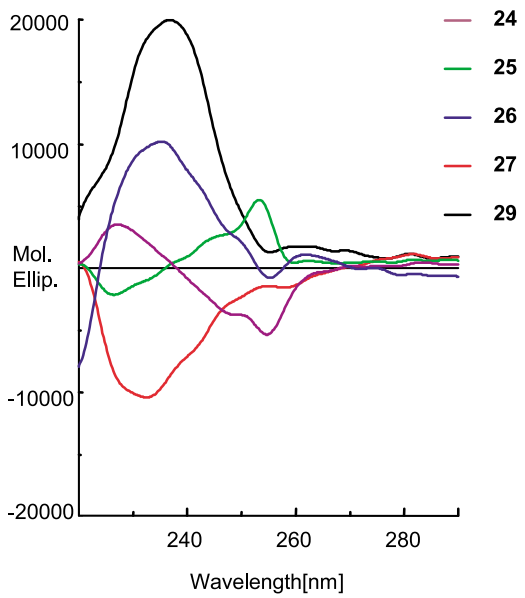


Figure 8. CD spectra of **24**–**29** in CH_3OH. (Mol. Ellip. in [10 deg cm^2 mol^{-1}]).

The ^1H NMR spectra were recorded in various solvents (DMSO-d_6, $CDCl_3$, CD_3CN and CD_3OD) and suggest, that the conformation of the dendrons is to some extent determined by the solvent. This is supported by ^1H NMR relaxation and ^1H-PGSE NMR measurements. ^1H-PGSE NMR measurements permit direct determination of molecular sizes in solution and indicate significant differences in CD_3CN and CD_3OD. T_1-relaxation times point to different segmental mobilities of the chiral units in different solvents. Analysis of the chiroptical properties show that observed changes in optical activity with increasing generation can be explained by constitutional effects of the dendron structure in CH_3OH but not in CH_3CN. The latter findings are in agreement with CD measurements which revealed a linear increase of the Cotton effects with increasing generation number for CH_3OH but not for CH_3CN as solvent. In CH_3CN the linear dependence of the Cotton effects on the number of benzene chromophores present was lost. Based on these results we conclude, that conformer equilibria within dendrons are very sensitive to the environmental conditions. The chiroptical data might then be explained by a stabilization of a chiral secondary structure in CH_3CN. However, based on the present data it cannot be decided whether this would be single stable conformers or an equilibrium between several forms including achiral folding motifs. In any case, further studies are necessary to rationalize the observed phenomena. In preliminary experiments we showed that chirality transfer to the focal group of the dendrons occurs. In future studies we will investigate whether the chirality is amplified by varying the conditions. Furthermore we are going to systematically replace the ω-aminocapronic acid spacer by other amino acids and peptides. The resulting depsipeptide dendrimers will be interesting mimics for peptide microenvironments found in nature.

4. Experimental

^1H and ^{13}C NMR spectra were recorded on JEOL GX 400, JEOL EX 400, and JEOL A 500. The chemical shifts are given in ppm relative to $SiMe_4$ or the solvent peak as standard reference. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Broad resonances are described as broad (b). PGSE NMR experiments were carried out on a JEOL A 500 equipped with an actively shielded gradient probehead (max. Gradient strength=1.4 T/m). A BPP-LED pulse sequence[18b,c] with a gradient pulse width δ=1 ms and a delay between the gradient pulses Δ=150 ms resp. Δ=75 ms was used. The gradient strength g was calibrated using the diffusion coefficient of HDO in D_2O.[24] ^1H NMR Relaxation times were recorded on a JEOL A 500 by the standard inversion recovery method. Mass spectra were measured with Micromas Zab Spec (FAB) on a Finnigan MAT 900 with 3-Nitrobenzylicalkohol as the matrix. IR spectra were recorded on Bruker FT-IR IFS 88. Circular dichroism (CD) measurements were carried out using optical grade solvents and quartz glass cuvettes with a 10 mm path length. Optical rotations were performed on a Schmidt&Haensch Digitalpolarimeter Polatronic E polarimeter. UV spectroscopy was performed using a UV-3102 by Shimadzu. Materials and solvents were obtained from commercial suppliers and were used without further purification. Products were isolated by flash column chromatography (FC) (silica gel 60, particle size 0.04–0.063 nm, Merck).

4.1. General procedure I for the synthesis of *R,R*- and *S,S*-dibenzyl 2,3-dihydroxysuccinate

Tartaric acid (1 mol) and p-toluenesulfonic acid (0.05 mol) were dissolved in 200 ml benzene and freshly distilled benzyl alcohol (2.1 mol) was added. The suspension was heated to 107°C and the evolving water was collected in a Dean Stark apparatus. After 24 h the mixture was allowed to cool down and 150 ml diethylether were added. The solution was washed three times with saturated aqueous sodium chloride (3×200 ml) and saturated aqueous sodium hydrogencarbonate (3×150 ml) and then dried over $MgSO_4$ and concentrated in vacuo.

4.2. General procedure II for the ester formation

The carboxylic acid (0.3 mol) and 4-dimethylaminopyridine (DMAP) (0.01 mol) and hydroxybenzotriazole (HOBt) (0.3 mol) were added to a solution of the alcohol (0.3 mol) in CH_2Cl_2 (150 ml). Dicyclohexyl carbodiimide (DCC) (0.35 mol) was added all at once at room temperature and after 20 min the first dicyclohexylurea (DCU) was formed. The suspension was stirred overnight. The precipitate of DCU was filtered and the solution washed with 10% aqueous hydrochloric acid HCl (1×100 ml) and with saturated aqueous sodium hydrogencarbonate ($NaHCO_3$) (3×150 ml) and concentrated in vacuo. The residue was dissolved in a little CH_2Cl_2 and hexane was added to precipitate a white solid. The product was filtered off, washed with further hexane and dried in vacuo.

4.3. General procedure III for the amide formation[11]

The diacid (2.5 mmol) was dissolved in CH_2Cl_2 (50 ml) and then triethylamine (NEt_3) (5 mmol), HOBt (5 mmol) and

the amine (5 mmol) were added. After cooling the solution to 0°C DCC (5 mmol) was added and the mixture was stirred for 24 h. The white precipitate of dicyclohexylurea (DCU) was filtered, the CH_2Cl_2 layer was washed once with 10% HCl (80 ml) and three times with a saturated aqueous solution of $NaHCO_3$ (3×50 ml). After removal of the solvent the crude product was purified by FC.

4.4. General procedure IV for the removal of the Bn ester

The Bn ester was dissolved in CH_3OH and 10 mass percent of Pd-C (10% Pd) were added. This suspension was subjected to hydrogenation until no more hydrogen was consumed. The Pd-C was filtered over aluminium oxide and CH_3OH was evaporated. The product was dried in vacuo.

4.5. General procedure V for the removal of the *tert*-butoxycarbonyl (BOC) protecting group[11]

The BOC-protected amine (5 mmol) was dissolved in CH_2Cl_2 (10 ml) and 99% trifluroacetic acid (10 ml) was added. After 45 min the reaction was complete and the solvent was evaporated. The viscous oil was dried for a further 24 h in vacuo.

4.5.1. 6-[(*tert*-Butoxycarbonyl)amino]hexanoic acid. 6-[(*tert*-Butoxycarbonyl)amino]hexanoic acid was prepared according to the literature procedure.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (m, 13H, BOC-CH_3, CH_2), 1.6 (quin., ^3J=7.5 Hz, 2H, CH_2), 2.31 (t, ^3J=7.2 Hz, CH_2COO), 3.07 (br, 2H, CH_2N), 4.56 (br, 1H, NH), 11.6 (br, 1H, COOH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.2, 26.1 (CH_2), 28.4 (BOC-CH_3), 29.4 (CH_2), 33.9 (CH_2COO), 40.3 (CH_2), 41.4 (CH_2N), 79.2 (BOC-C), 156.1 (BOC-C=O), 179.2 (COOH); MS (FAB): *m/z* (%): 463 (16) $[2\times M]^+$, 232 (40) $[M+H]^+$, 176 (100) $[M-t\text{-Butyl}]^+$; $C_{11}H_{21}O_4N$ (231.3): calcd: C 57.13, H 9.15, N 6.02; found: C 57.11, H 9.40, N 6.13.

4.5.2. *R*,*R*-Dibenzyl 2,3-dihydroxysuccinate (3). Compound **3** was synthesized according to general procedure **I** with *R*,*R*-tartaric acid (**1**) (150.09 g, 1 mol). Yield 303.8 g, 0.92 mol, 92%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.3 (br, 2H, OH), 4.60 (d, ^3J=3.6 Hz, 2H, *CH), 5.22 (d, ^2J=12 Hz, 2H, CH_2-Bn), 5.29 (d, ^2J=12 Hz, 2H, CH_2-Bn), 7.36 (m, 10H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 68.0 (CH_2-Bn), 72.1 (*CH), 128.3, 128.4, 128.7 (Ph), 134.7 (q-Ph), 171.3 (C=O); MS (FAB): *m/z* (%): 353 (9) $[M+Na]^+$, 331 (24) $[M+H]^+$, 181 (100); $C_{18}H_{18}O_6$ (330.3): calcd: C 65.45, H 5.49 found: C 65.11, H 5.40; $[\alpha]_D^{20}$=+16.6 (*c*=1.290, CH_2Cl_2).

4.5.3. *S*,*S*-Dibenzyl 2,3-dihydroxysuccinate (4). Compound **4** was synthesized according to general procedure **I** with *S*,*S*-tartaric acid (**2**) (50 g, 0.33 mol). Yield 99.2 g, 0.3 mol, 91%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (d, ^3J=7 Hz, 2H, OH), 4.60 (d, ^3J=7 Hz, 2H, *CH), 5.22 (d, ^2J=12 Hz, 2H, CH_2-Bn), 5.29 (d, ^2J=12 Hz, 2H, CH_2-Bn), 7.35 (m, 10H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 68.0 (CH_2-Bn), 72.1 (*CH), 128.3, 128.4, 128.6 (Ph), 134.7 (q-Ph), 171.3 (C=O); MS (FAB): *m/z* (%): 353 (15) $[M+Na]^+$, 331 (5) $[M+H]^+$, 181 (100); $C_{18}H_{18}O_6$ (330.3): calcd: C 65.45, H 5.49 found: C 65.31, H 5.30; $[\alpha]_D^{20}$=-16.2 (*c*=1.204, CH_2Cl_2).

4.5.4. *R*,*R*-Dibenzyl 2-(benzoyloxy) 3-hydroxysuccinate (5). Compound **5** was synthesized according to general procedure **II** with *R*,*R*-dibenzyl 2,3-dihydroxysuccinate (**3**) (99.3 g; 0.3 mol) and benzoic acid (36.7 g; 0.3 mol). Yield 49.76 g, 0.11 mol, 38%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.27 (d, ^3J=7.6 Hz, 1H, OH), 4.89 (dd, ^3J=7.6 Hz, ^3J=2.4 Hz, 1H, *CH), 5.10 (d, ^2J=12 Hz, 2H, CH_2-Bn), 5.23 (d, ^2J=12 Hz, 2H, CH_2-Bn), 5.67 (d, ^3J=2.4 Hz, 1H, *CH), 7.10 (m, 3H, Bn-Ph), 7.18 (m, 2H, Bn-Ph), 7.31 (m, 5H, Bn-Ph), 7.37 (m, 2H, Bz-Ph), 7.56 (m, 1H, Bz-Ph), 7.90 (m, 2H, Bz-Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 67.6, 68.3 (CH_2-Bn), 70.6, 70.7 (*CH), 128.1, 128.3, 128.4, 128.44, 128.5, 128.6, 128.9 (Ph), 133.5, 134.3, 134.9 (q-Ph), 165.0, 166.3, 170.7 (C=O); MS (FAB): *m/z* (%): 435 (85) $[M+H]^+$, 307 (41), 182 (100); $C_{25}H_{22}O_7$ (434.3): calcd: C 69.12, H 5.10 found: C 69.11, H 5.30; $[\alpha]_D^{20}$=+37.1 (*c*=1.1400, CH_2Cl_2).

4.5.5. *S*,*S*-Dibenzyl 2-(benzoyloxy) 3-hydroxysuccinate (6). Compound **6** was synthesized according to general procedure **II** with *S*,*S*-dibenzyl 2,3-dihydroxysuccinate (**4**) (99.3 g; 0.3 mol) and benzoic acid (36.7 g; 0.3 mol). Yield 26.95 g, 0.062 mol, 31%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (d, ^3J=8 Hz, 1H, OH), 4.89 (dd, ^3J=8 Hz, ^3J=3 Hz, 1H, *CH), 5.11 (d, ^2J=12 Hz, 2H, CH_2-Bn), 5.21 (d, ^2J=12 Hz, 2H, CH_2-Bn), 5.67 (d, ^3J=3 Hz, 1H, *CH), 7.10 (m, 3H, Bn), 7.19 (m, 2H, Bn), 7.32 (m, 5H, Bn), 7.37 (m, 2H, Bz), 7.56 (m, 1H, Bz), 7.90 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 67.4, 68.2 (CH_2-Bn), 70.6, 70.7 (*CH), 128.1, 128.2, 128.4, 128.45, 128.5, 128.7, 128.9 (Ph), 133.5, 134.3, 134.9 (q-Ph), 164.9, 166.3, 170.9 (C=O); MS (FAB): *m/z* (%): 435 (75) $[M+H]^+$, 307 (41), 182 (100); $C_{25}H_{22}O_7$ (434.3): calcd: C 69.12, H 5.10 found: C 69.21, H 4.95; $[\alpha]_D^{20}$=-37.4 (*c*=1.302, CH_2Cl_2).

4.5.6. Compound 7, dendron first generation. Compound **7** was synthesized according to general procedure **II** with 6-[(*tert*-butoxycarbonyl)amino]hexanoic acid (13.96 g, 0.06 mol) and *R*,*R*-dibenzyl 2-(benzoyloxy) 3-hydroxy-succinate (**5**) (26.21 g, 0.06 mol). The white precipitate was filtered off and the organic phase was evaporated to provide product.

Yield 29.5 g, 0.046 mol, 76%, viscous, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 15H, BOC-CH_3, CH_2), 2.14 (quin, *J*=7.6 Hz, 1H, CHCOO), 2.27 (quin, *J*=7.6 Hz, 1H, CHCOO), 3.05 (m, 2H, CH_2N), 4.49 (br, 1H, NH), 5.03 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.10 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.15 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.20 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.80 (d, ^3J=2.8 Hz, 1H, *CH), 5.91 (d, ^3J=2.8 Hz, 1H, *CH), 7.09 (m, 3H, Bn), 7.10 (m, 2H, Bn), 7.29 (m, 5H, Bn), 7.37 (m, 2H, Bz), 7.54 (m, 1H, Bz), 7.92 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.2, 26.0 (CH_2), 28.4 (BOC-CH_3), 29.6 (CH_2), 29.6 (CH_2COO), 40.3 (CH_2N), 67.7, 67.8 (CH_2-Bn), 70.7, 71.2 (*CH), 79.0 (q-BOC), 128.3, 128.4, 128.5, 128.5, 128.6, 130.1 (Ph), 133.6, 134.5, 134.8 (q-Ph), 155.9 (BOC-C=O), 165.0, 165.6, 165.7, 172.1 (C=O); MS (FAB): *m/z* (%): 648 (12) $[M+H]^+$, 592 (11) $[M-t\text{-Butyl}]^+$, 548 (100) [M-BOC]$^+$; $C_{36}H_{41}O_{10}N$ (647.4): calcd: C 66.80, H 6.38, N 2.16; found:

C 67.11, H 6.40, N 2.23; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 263, 231 (12800); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (12700); $[\alpha]_D^{20}$=+34.4 (c=1.202, CH_2Cl_2).

4.5.7. Compound 8, dendron first generation. Compound **8** was synthesized according to general procedure **II** with 6-[(*tert*-butoxycarbonyl)amino]hexanoic acid (13.96 g, 0.06 mol) and *S*,*S*-dibenzyl 2-(benzoyloxy) 3-hydroxy-succinate (**6**) (26.21 g, 0.06 mol). The white precipitate was filtered off and the organic phase was evaporated to provide product.

Yield 29.2 g, 0.045 mol, 75%, viscous, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (m, 15H, BOC-CH_3, CH_2), 2.20 (quin, J=7.6 Hz, 1H, CHCOO), 2.27 (quin, J=7.6 Hz, 1H, CHCOO), 3.06 (m, 2H, CH_2N), 4.49 (br, 1H, NH), 5.03 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.11 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.15 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.21 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.80 (d, ^3J=2.8 Hz, 1H, *CH), 5.89 (d, ^3J=2.8 Hz, 1H, *CH), 7.09 (m, 3H, Bn), 7.15 (m, 2H, Bn), 7.26 (m, 5H, Bn, 7.39 (m, 2H, Bz), 7.54 (m, 1H, Bz), 7.93 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.5, 25.9 (CH_2), 28.2 (BOC-CH_3), 29.6 (CH_2), 29.6 (CH_2COO), 40.1 (CH_2N), 67.8, 67.9 (CH_2-Bn), 70.7, 71.2 (*CH), 79.4 (q-BOC), 128.3, 128.4, 128.5, 128.5, 128.6, 130.3 (Ph), 133.7, 134.5, 134.8 (q-Ph), 155.6 (BOC-C=O), 164.8, 165.6, 165.7, 172.1 (C=O); MS (FAB): *m*/*z* (%): 648 (15) $[M+H]^+$, 592 (10) $[M-t\text{-Butyl}]^+$, 548 (100) $[M-BOC]^+$; $C_{36}H_{41}O_{10}N$ (647.4): calcd: C 66.80, H 6.38, N 2.16; found: C 66.53, H 6.56, N 2.26; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 263, 231 (12800); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (12700); $[\alpha]_D^{20}$=-35.5 (c=1.312, CH_2Cl_2).

4.5.8. Compound 9, dendron first generation (NH_2). Compound **9** was synthesized according to general procedure **V** with compound **7** (1.7 g; 2.62 mmol). Yield 1.72 g, 2.598 mmol, 99%, colorless, viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 2.15 (quin, J=7.8 Hz, 1H, CHCOO), 2.28 (quin, J=7.8 Hz, 1H, CHCOO), 2.93 (br, 2H, CH_2N), 5.04 (d, ^2J=12.4 Hz, 1H, CH_2-Bn), 5.080 (d, ^2J=12.4 Hz, 1H, CH_2-Bn), 5.12 (d, ^2J=12.4 Hz, 1H, CH_2-Bn), 5.29 (d, ^2J=12.4 Hz, 1H, CH_2-Bn), 5.80 (d, ^3J=2.8 Hz, 1H, *CH), 5.91 (d, ^3J=2.8 Hz, 1H, *CH), 7.09 (m, 4H, Ph), 7.21 (m, 4H, Ph), 7.49 (m, 5H, Ph), 7.89 (m, 2H, Ph), 8.21 (br, 2H, NH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 23.4, 25.1, 26.7 (CH_2), 32.8 (CH_2COO), 39.9 (CH_2N), 67.8, 68.1 (CH_2-Bn), 70.8, 71.1 (*CH), 115.0 (q, ^1J(C,F)=284 Hz, TFA), 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 129.9 (Ph), 133.8, 134.3, 134.7 (q-Ph), 163 (q, ^2J(C,F)=44 Hz, TFA), 165.0, 165.7, 165.8, 172.1 (C=O); MS (FAB): *m*/*z* (%): 1095 (4) $[2^*M^+]$, 548 (100) $[M+H]^+$, 458 (5) $[M-Bn]^+$, 431 (23).

4.5.9. Compound 10, dendron first generation (NH_2). Compound **10** was synthesized according to general procedure **V** with compound **8** (4.6 g; 7.1 mmol). Yield 4.65 g, 7.0 mmol, 99%, colorless, viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 2H, CH_2), 1.54 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 2.17 (quin, J=7.8 Hz, 1H, CHCOO), 2.28 (quin, J=7.8 Hz, 1H, CHCOO), 2.97 (m, 2H, CH_2N), 5.04 (d, ^2J=12 Hz, 1H, Bn), 5.09 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.13 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.25 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.81 (d, ^3J=3 Hz, 1H, *CH), 5.92 (d, ^3J=3 Hz, 1H, *CH), 7.09 (m, 5H, Bn), 7.29 (m, 5H, Bn), 7.39 (m, 2H, Bz), 7.57 (m, 1H, Bz), 7.90 (m, 2H, Bz), 10.1 (br, 2H, NH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 23.4, 25.1, 26.7 (CH_2), 32.8 (CH_2COO), 39.9 (CH_2N), 67.8, 68.1 (CH_2-Bn), 70.8, 71.1 (*CH), 115.0 (q, ^1J(C,F)=284 Hz, TFA), 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 129.9 (Ph), 133.8, 134.3, 134.7 (q-Ph), 163 (q, ^2J(C,F)=44 Hz, TFA), 165.0, 165.7, 165.8, 172.1 (C=O); MS (FAB): *m*/*z* (%): 548 (100) $[M]^+$, 458 (5) $[M-Bn]^+$, 431 (23).

4.5.10. Compound 11, dendron first generation (COOH). Compound **11** was synthesized according to general procedure **IV** with compound **7** (2.97 g; 4.59 mmol) and 10% Pd/C (122 mg) in CH_3OH (250 ml). Yield 2.13 g, 4.54 mmol, 99%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (br, 13H, CH_2, BOC-CH_3), 1.62 (br, 2H, CH_2), 2.35 (m, 1H, CHCOO), 2.40 (br, 1H, CHCOO), 2.97 (br, 1H, CH_2N), 3.12 (br, 1H, CH_2N), 5.86 (br, 2H, *CH), 6.23 (b, 1H, NH), 7.38 (m, 2H, Bz), 7.52 (m, 1H, q-Bz), 8.01 (m, 2H, Bz), 9.5 (br, 2H, COOH); ^{13}C NMR (100.6 MHz, DMSO): δ 24.4, 25.8 (CH_2), 28.6 (BOC-CH_3), 29.4 (CH_2COO), 33.5 (CH_2NH), 71.1, 71.7 (*CH), 78.0 (q-BOC), 128.7, 129.4, 129.7 (Ph), 134.5 (q-Ph), 156.1 (BOC-C=O), 165.1, 167.6, 167.8, 172.5 (C=O); MS (FAB): *m*/*z* (%): 600 (9) $[M+Cs]^+$, 506 (30) $[M+K]^+$, 490 (89) $[M+Na]^+$, 468 (48) $[M+H]^+$, 412 (100) $[M-t\text{-Butyl}]^+$; $C_{22}H_{29}O_{10}N$ (467.4): calcd: C 56.53, H 6.25, N 2.99; found: C 57.03, H 6.56, N 2.36.

4.5.11. Compound 12, dendron first generation (COOH). Compound **12** was synthesized according to general procedure **IV** with compound **8** (3.86 g; 5.97 mmol) and 10% Pd/C (200 mg) in CH_3OH (300 ml). Yield 2.59 g, 5.55 mmol, 93%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (br, 13H, CH_2, BOC-CH_3), 1.67 (br, 2H, CH_2), 2.27 (m, 1H, CHCOO), 2.43 (br, 1H, CHCOO), 2.97 (br, 1H, CH_2N), 3.19 (br, 1H, CH_2N), 5.79 (br, 2H, *CH), 6.22 (br, 1H, NH), 7.38 (m, 2H, Bz), 7.53 (m, 1H, q-Bz), 8.07 (m, 2H, Bz), 9.51 (br, 2H, COOH); ^{13}C NMR (100.6 MHz, DMSO): δ 24.5, 25.8 (CH_2), 28.3 (BOC-CH_3), 29.6 (CH_2COO), 33.8 (CH_2NH), 70.7, 71.3 (*CH), 80.8 (q-BOC), 128.4, 128.7, 130.1 (Ph), 133.5 (q-Ph), 157.1 (BOC-C=O), 165.2, 167.6, 167.8, 172.3 (C=O); MS (FAB): *m*/*z* (%): 506 (42) $[M+K]^+$, 490 (37) $[M+Na]^+$, 468 (38) $[M+H]^+$, 412 (50) $[M-t\text{-Butyl}]^+$, 368 (100) $[M-BOC]^+$; $C_{22}H_{29}O_{10}N$ (467.4): calcd: C 56.53, H 6.25, N 2.99; found: C 57.12, H 6.47, N 2.56.

4.5.12. Compound 13, dendron second generation. Compound **13** was synthesized according to general procedure **III** with compound **12** (1.03 g; 2.2 mmol) and compound **9** (TFA-adduct) (2.81 g; 4.4 mmol). The crude product was purified by column chromatography (silica, EtOAc/hexane, 1:1; R_f=0.26).

Yield 800 mg, 0.52 mmol, 24%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (m, 27H, CH_2, BOC-CH_3), 2.16 (m, 4H, CH_2COO), 2.38 (m, 2H, CH_2COO), 3.03 (m, 2H, CH_2N), 3.21 (m, 4H, CH_2N), 4.64 (br, 1H, NH), 5.03 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.05 (d, ^2J=6 Hz, 1H, CH_2-Bn),

5.09 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.11 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.17 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.19 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.22 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.25 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.75 (d, ^3J=3 Hz, 1H, *CH), 5.77 (d, ^3J=3 Hz, 1H, *CH), 5.80 (d, ^3J=3 Hz, 1H, *CH), 5.82 (d, ^3J=3 Hz, 1H, *CH), 5.89 (d, ^3J=3 Hz, 1H, *CH), 5.91 (d, ^3J=3 Hz, 1H, *CH), 6.25 (br, 2H, NH), 7.09 (m, 6H, Bn), 7.15 (m, 4H, Bn), 7.28 (m, 10H, Bn), 7.40 (m, 6H, Bz), 7.55 (m, 3H, q-Bz), 7.91 (m, 4H, Bz), 8.01 (m, 2H, Bz); ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 23.9, 24.0, 24.3, 25.8, 25.9, 26.0 (CH_2), 28.4 (BOC-CH_3), 28.8, 28.9, 29.5 (CH_2), 33.0, 33.1, 33.7 (CH_2COO), 39.2, 39.3, 40.2 (CH_2N), 67.7, 67.8, 67.9 (CH_2-Bn), 70.7, 71.2, 71.25, 72.2, 72.7 (*CH), 79.0 (q-BOC), 128.3, 128.5, 128.6, 128.7, 129.9, 130.0, 133.6, 133.9, 134.5, 134.8 (Ph), 155.9 (BOC-C=O), 163.6, 164.9, 165.5, 165.6, 165.7, 166.0, 166.1, 171.8, 172.0 (C=O); MS (FAB): *m/z* (%): 1526 (2) $[M+H]^+$, 1426 (79) $[M-BOC]^+$, 1336 (9) $[M-BOC\text{-}Bn]^+$, 548 (39); $C_{84}H_{91}O_{24}N3$ (1526.6): calcd: C 66.09, H 6.00, N 2.75; found: C 65.56, H 6.16, N 2.83; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 269, 231 (37625); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (39700); $[\alpha]_D^{20}$=+22.3 (*c*=1.100, CH_2Cl_2).

4.5.13. Compound 14, dendron second generation. Compound **14** was synthesized according to general procedure **III** with compound **12** (1.64 g; 3.5 mmol) and compound **10** (TFA-adduct) (2.81 g; 4.4 mmol). The crude product was purified by column chromatography (silica, EtOAc/hexane, 1:1; R_f=0.26).

Yield 1.2 g, 0.78 mmol, 23%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 27H, CH_2, BOC-CH_3), 2.15 (m, 4H, CH_2COO), 2.35 (m, 2H, CH_2COO), 3.03 (m, 2H, CH_2N), 3.21 (m, 4H, CH_2N), 4.62 (br, 1H, NH), 5.03 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.06 (d, ^2J=6 Hz, 1 H, CH_2-Bn), 5.09 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.12 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.16 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.19 (d, ^2J=4 Hz, 1H, CH_2-Bn), 5.21 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.25 (d, ^2J=4 Hz, 1H, CH_2-Bn), 5.72 (d, ^3J=3 Hz, 1H, *CH), 5.77 (d, ^3J=3 Hz, 1H, *CH), 5.80 (d, ^3J=3 Hz, 1H, *CH), 5.82 (d, ^3J=3 Hz, 1H, *CH), 5.89 (d, ^3J=3 Hz, 1H, *CH), 5.91 (d, ^3J=3 Hz, 1H, *CH), 6.24 (br, 2H, NH), 7.09 (m, 6H, Bn), 7.15 (m, 4H, Bn), 7.28 (m, 10H, Bn), 7.42 (m, 6H, Bz), 7.56 (m, 3H, q-Bz), 7.91 (m, 4H, Bz), 8.02 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 23.9, 24.0, 24.3, 25.8, 25.9, 26.0 (CH_2), 28.4 (BOC-CH_3), 28.8, 28.9, 29.5 (CH_2), 33.1, 33.2, 33.7 (CH_2COO), 39.2, 39.3, 40.1 (CH_2N), 67.7, 67.8, 67.9 (CH_2-Bn), 70.7, 71.2, 71.3, 72.2, 72.7 (*CH), 78.9 (q-BOC), 128.3, 128.43, 128.47, 128.5, 128.6, 129.9, 130.0, 133.6, 133.4, 134.5, 134.8 (Ph), 155.9 (BOC-C=O), 164.9, 165.5, 165.6, 165.7, 166.0, 166.1, 171.8, 172.0 (C=O); MS (FAB): *m/z* (%): 1526 (5) $[M+H]^+$, 1426 (100) $[M-BOC]^+$, 1336 (11) $[M-BOC\text{-}Bn]^+$; $C_{84}H_{91}O_{24}N_3$ (1526.6): calcd: C 66.09, H 6.00, N 2.75; found: C 64.96, H 6.13, N 2.76; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 263, 231 (37600); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (39000); $[\alpha]_D^{20}$=-21.1 (1.092, CH_2Cl_2).

4.5.14. Compound 15, dendron second generation. Compound **15** was synthesized according to general procedure **III** with compound **12** (0.7 g; 1.5 mmol) and compound **11** (TFA-adduct) (1.64 g; 3.0 mmol). The crude product was purified by column chromatography (silica, EtAc/hexane, 1:1; R_f=0.15).

Yield 1.03 g, 0.675 mmol, 45%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (m, 27H, CH_2, BOC-CH_3), 2.17 (m, 4H, CH_2COO), 2.37 (m, 2H, CH_2COO), 3.03 (m, 2H, CH_2N), 3.20 (m, 4H, CH_2N), 4.62 (br, 1H, NH), 5.02 (d, ^2J=9 Hz, 1H, CH_2-Bn), 5.05 (d, ^2J=9 Hz, 1H, CH_2-Bn), 5.09 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.12 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.16 (d, ^2J=8 Hz, 1H, CH_2-Bn), 5.19 (d, ^2J=8 Hz, 1H, CH_2-Bn), 5.22 (d, ^2J=10 Hz, 1H, CH_2-Bn), 5.25 (d, ^2J=10 Hz, 1H, CH_2-Bn), 5.72 (d, ^3J=3 Hz, 1H, *CH), 5.77 (d, ^3J=3 Hz, 1H, *CH), 5.80 (d, ^3J=5 Hz, 1H, *-CH), 5.82 (d, ^3J=5 Hz, 1H, *CH), 5.89 (d, ^3J=3 Hz, 1H, *CH), 5.91 (d, ^3J=3 Hz, 1H, *CH), 6.24 (br, 2H, NH), 7.10 (m, 6H, Bn), 7.15 (m, 4H, Bn), 7.28 (m, 10H, Bn), 7.38 (m, 6H, Bz), 7.55 (m, 3H, q-Bz), 7.91 (m, 4H, Bz), 8.01 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.0, 24.1, 24.3, 24.9, 25.6, 25.9 (CH_2), 28.4 (BOC-CH_3), 28.9, 29.0, 29.6 (CH_2), 33.1, 33.2, 33.7 (CH_2COO), 39.3, 39.31, 40.2 (CH_2N), 49.1, 67.7, 67.8 (CH_2-Bn), 70.7, 71.2, 72.3, 72.7 (*CH), 78.9 (q-BOC), 128.3, 128.4, 128.5, 128.6, 128.7, 129.9, 130.0, 133.6, 133.9, 134.5, 134.8 (Ph), 155.9 (BOC-C=O), 165.0, 165.6, 165.7, 166.0, 166.1, 171.8, 172.0 (C=O); MS (FAB): *m/z* (%): 1527 (2) $[M+H]^+$, 1427 (100) $[M-BOC]^+$, 1336 (9) $[M-BOC\text{-}Bn]^+$, 548 (9); $C_{84}H_{91}O_{24}N3$ (1526.6): calcd: C 66.09, H 6.00, N 2.75; found: C 65.86, H 6.13, N 2.86; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 263, 231 (37600); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (39100); $[\alpha]_D^{20}$=+35.6 (*c*=0.926, CH_2Cl_2).

4.5.15. Compound 16, dendron second generation (NH_2). Compound **16** was synthesized according to general procedure **V** with compound **13** (700 mg; 4.6 mmol) and 99% trifluoroacetic acid (8 ml) in CH_2Cl_2 (8 ml).

Yield 710 mg, 4.58 mmol, 99%, viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.41 (m, 18H, CH_2), 2.07 (m, 4H, CH_2COO), 2.25 (m, 2H, CH_2COO), 2.97 (br, 2H, CH_2N), 3.19 (m, 4H, CH_2N), 5.01 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.04 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.09 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.12 (d, ^2J=6 Hz, 1H, CH_2-Bn), 5.17 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.21 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.72 (m, 2H, *CH), 5.80 (m, 2H, *CH), 5.91 (m, 2H, *CH), 7.2 (m, 26H, Ph), 7.91 (m, 9H, Ph); ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 23.4, 23.7, 23.8, 23.9, 24.5, 25.4, 25.7, 28.3, 28.5 (CH_2), 32.5, 33.0, 33.1 (CH_2COO), 39.6, 39.7, 40.0 (CH_2N), 67.8, 67.9 (CH_2-Bn), 70.8, 71.2, 72.3, (*CH), 115.0 (q, ^1J(C,F)=284 Hz, TFA), 127.8, 128.2, 128.4, 128.5, 128.51, 128.6, 128.8, 129.8, 129.9, 133.7, 134.4, 134.7 (Ph), 163 (q, ^2J(C,F)=44 Hz, TFA), 160.2, 164.9, 165.0, 165.7, 167.4, 167.5, 171.8, 172.2, 172.3 (C=O); MS (FAB): *m/z* (%): 1427 (100) $[M+H]^+$, 1337 (8) $[M-Bn]^+$, 912 (30).

4.5.16. Compound 19, dendron third generation. Compound **19** was synthesized according to general procedure **III** with compound **16** (TFA adduct) (570 mg; 0.4 mmol) and with compound **11** (94 mg; 0.2 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 25:1; R_f=0.15).

Yield 230 mg, 0.07 mmol, 18%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (m, 47H, CH_2, BOC-CH_3), 1.66

(s, 4H), 2.20 (m, 14H, CH_2COO), 3.16 (m, 14H, CH_2N), 4.77 (br, 1H, NHBOC), 5.15 (m, 16H, CH_2-Bn), 5.85 (m, 14H, *CH), 6.50 (br, 4H, NH), 6.61 (br, 2H, NH), 7.07 (m, 12H, Ph), 7.14 (m, 8H, q-Bn), 7.27 (m, 20H, Bn), 7.37 (m, 14H, Bz), 7.53 (m, 7H, q-Bz), 7.90 (m, 8H, Bz), 8.00 (m, 6H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.0, 24.3, 24.9, 25.6, 25.9 (CH_2), 28.4 (BOC-CH_3), 28.8, 28.9, 29.5 (CH_2), 33.1, 33.2, 33.6, 33.7, 33.9 (CH_2COO), 39.0, 39.3, 40.2 (CH_2N), 67.7, 67.8 (CH_2-Bn), 70.7, 71.1, 71.2, 72.4, 72.8, 72.9 (*CH), 78.9 (q-BOC), 128.3, 128.4, 128.5, 128.6, 128.7, 129.9, 130.0, 133.7, 133.9, 134.5, 134.7 (Ph), 156.6 (BOC-C=O), 165.0, 165.5, 165.7, 166.1, 171.9, 172.1 (C=O); MS (FAB): *m/z* (%): 3183 (49) $[M-BOC]^+$, 1832 (88), 1427 (100); $C_{180}H_{191}O_{52}N_7$ (3284.3): calcd: C 65.81, H 5.87, N 2.99; found: C 65.04, H 6.12, N 3.38; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 231 (83250); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 268, 231 (81600); $[\alpha]_D^{20}$=+12.7 (*c*=1.060, CH_2Cl_2).

4.5.17. Compound 20, dendron third generation. Compound **20** was synthesized according to general procedure **III** with compound **17** (TFA adduct) (820 mg; 0.5 mmol) and with compound **12** (117 mg; 0.2 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 25:1; R_f=0.15).

Yield 264 mg, 0.07 mmol, 17%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (m, 47H, CH_2, BOC-CH_3), 1.83 (s, 4H), 2.20 (m, 14H, CH_2COO), 3.17 (m, 14H, CH_2N), 4.77 (br, 1H, NHBOC), 5.05 (m, 8H, CH_2-Bn), 5.20 (m, 8H, CH_2-Bn), 5.74 (m, 10H, *CH), 5.89 (m, 4H, *CH), 6.50 (br, 4H, NH), 6.61 (br, 2H, NH), 7.07 (m, 12H, Ph), 7.14 (m, 8H, q-Bn), 7.26 (m, 20H, Bn), 7.37 (m, 14H, Bz), 7.53 (m, 7H, q-Bz), 7.90 (m, 8H, Bz), 8.01 (m, 6H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 23.8, 23.9, 24.0, 24.2, 25.7, 25.8, 25.9 (CH_2), 28.3 (BOC-CH_3), 28.6, 28.7, 28.8, 29.4 (CH_2), 32.9, 33.0, 33.4, 33.5, 33.6 (CH_2COO), 38.9, 39.0, 39.2, 39.3 (CH_2N), 67.7, 67.8 (CH_2-Bn), 70.7, 71.1, 71.2, 72.3, 72.7, 72.9 (*CH), 78.9 (q-BOC), 128.2, 128.3, 128.4, 128.45, 128.5, 128.6, 128.7, 129.8, 129.9, 133.6, 133.8, 133.9, 134.4, 134.7 (Ph), 156.0 (BOC-C=O), 164.9, 164.97, 165.5, 165.6, 166.1, 171.9, 171.92, 172.0 (C=O); MS (FAB): *m/z* (%): 3283 (1) $[M+H]^+$, 3183 (100) $[M-BOC]^+$, 3093 (8) $[M-BOC-Bn]^+$, 1889 (10), 1313 (10); $C_{180}H_{191}O_{52}N_7$ (3284.3): calcd: C 65.81, H 5.87, N 2.99; found: C 65.36, H 5.88, N 2.67; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 231 (83250); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 268, 231 (81600); $[\alpha]_D^{20}$=-12.5 (*c*=0.8400, CH_2Cl_2).

4.5.18. Compound 21, dendron third generation. Compound **21** was synthesized according to general procedure **III** with compound **18** (TFA adduct) (330 mg; 0.2 mmol) and with compound **11** (47 mg; 0.1 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 25:1; R_f=0.12).

Yield 234 mg, 0.07 mmol, 71%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (m, 47H, CH_2, BOC-CH_3), 1.74 (s, 4H), 2.20 (m, 14H, CH_2COO), 3.15 (m, 14H, CH_2N), 4.77 (br, 1H, NHBOC), 5.15 (m, 16H, CH_2-Bn), 5.71 (m, 4H, *CH), 5.78 (m, 8H, *CH), 5.83 (m, 4H, *CH), 6.50 (br, 6H, NH), 7.08 (m, 12H, Ph), 7.14 (m, 8H, q-Bn), 7.26 (m, 20H, Bn), 7.37 (m, 14H, Bz), 7.53 (m, 7H, q-Bz), 7.90 (m, 8H, Bz), 8.01 (m, 6H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.0, 24.3, 24.9, 25.6, 25.8, 25.9 (CH_2), 28.3 (BOC-CH_3), 28.6, 28.7, 28.8, 29.1, 29.5 (CH_2), 33.1, 33.7, 33.9 (CH_2COO), 38.9, 39.0, 39.2, 39.3 (CH_2N), 67.7, 67.8 (CH_2-Bn), 70.7, 71.1, 71.2, 72.3, 72.8, 73.1 (*CH), 128.3, 128.4, 128.5, 128.6, 130.0, 128.6, 133.6, 133.8, 133.9, 134.4, 134.7 (Ph), 156.7 (BOC-C=O), 164.9, 165.5, 165.7, 166.1, 166.2, 168.5, 171.9, 172.0 (C=O); MS (FAB): *m/z* (%): 3283 (1) $[M]^+$, 3183 (65) $[M-BOC]^+$, 3093 (3) $[M-BOC-Bn]^+$, 1313 (62), 548 (100); $C_{180}H_{191}O_{52}N_7$ (3284.3): calcd: C 65.81, H 5.87, N 2.99; found: C 65.26, H 5.88, N 2.87; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 231 (83200); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 268, 231 (81600); $[\alpha]_D^{20}$=+30.9 (*c*=0.500, CH_2Cl_2).

4.5.19. Compound 22, model compound. Compound **22** was synthesized according to general procedure **III** with compound **11** (185 mg; 0.39 mmol) and benzyl 6-aminohexanoate[11] (311 mg; 0.8 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 20:1; R_f=0.36).

Yield 157 mg, 0.18 mmol, 45%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 27H, BOC-CH_3, CH_2), 2.30 (m, 6H, CHCOO), 3.15 (m, 6H, CH_2N), 4.61 (br, 1H, NH), 5.06 (d, ^2J=8 Hz, 4H, CH_2-Bn), 5.72 (d, ^3J=4 Hz, 1 H, *CH), 5.81 (d, ^3J=4 Hz, 1H, *CH), 7.31 (m, 10H, Ph-Bn), 7.44 (m, 2H, Ph-Bz), 7.55 (m, 1H, Bz), 8.01 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.3, 24.4, 26.0, 26.1, 26.2 (CH_2), 28.4 (BOC-CH_3), 28.9, 29.0, 29.6, 29.6, 33.7, 33.9, 34.0, 39.3, 39.4, 40.3 (CH_2), 66.1, 72.2, 72.8, 79.0 (q-BOC), 118.5, 128.2, 128.5, 128.6, 128.7, 129.9, 133.9, 136.0, 155.9 (BOC-C=O), 165.0, 166.1, 171.9, 173.1 (C=O); MS (FAB): *m/z* (%): 874 (40) $[M+H]^+$, 774 (100) $[M-BOC]^+$; $C_{48}H_{63}O_{12}N_3$ (874.0): calcd: C 65.96, H 7.27, N 4.81; found: C 65.56, H 6.88, N 4.77; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 263, 231 (12900); UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (13000); $[\alpha]_D^{20}$=-16.0 (*c*=0.123, CH_2Cl_2).

4.5.20. Compound 23, model compound. Compound **23** was synthesized according to general procedure **III** with compound **12** (604 mg; 1.29 mmol) and benzyl 6-aminohexanoate[11] (1061 mg; 2.58 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 20:1; R_f=0.36).

Yield 980 mg, 1.12 mmol, 87%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (m, 27H, BOC-CH_3, CH_2), 2.31 (m, 6H, CHCOO), 3.15 (m, 6H, CH_2N), 4.65 (br, 1H, NH), 5.07 (d, ^2J=8 Hz, 4H, CH_2-Bn), 5.73 (d, ^3J=4 Hz, 1H, *CH), 5.81 (d, ^3J=4 Hz, 1H, *CH), 7.32 (m, 10H, Ph-Bn), 7.41 (m, 2H, Ph-Bz), 7.55 (m, 1H, Bz), 8.01 (m, 2H, Bz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.3, 24.4, 24.9, 26.0, 26.1 (CH_2), 28.4 (BOC-CH_3), 28.9, 29.0, 29.5, 33.7, 33.9, 34.0, 39.2, 39.4, 40.3 (CH_2), 66.1, 72.2, 72.8, 79.0 (q-BOC), 128.2, 128.5, 128.6, 128.7, 129.9, 133.9, 136.0, 155.9 (BOC-C=O), 165.0, 166.1, 171.9, 173.2 (C=O); MS (FAB): *m/z* (%): 874 (40) $[M+H]^+$, 774 (100) $[M-BOC]^+$; $C_{48}H_{63}O_{12}N_3$ (874.0): calcd: C 65.96, H 7.27, N 4.81; found: C 66.34, H 7.58, N 4.92; UV/Vis (CH_3CN) λ_{max} (ε) (nm): 274, 268, 263, 231 (12900);

UV/Vis (CH_3OH) λ_{max} (ε) (nm): 274, 268, 263, 231 (13000); $[\alpha]_D^{20}$=+16.0 (c=0.123, CH_2Cl_2).

4.5.21. Compound 24, dendron first generation (anthracene). Compound **24** was synthesized according to general procedure **III** with compound **9** (TFA-adduct) (1.98 g; 3 mmol) and 9-anthracenecarboxylic acid (0.67 g; 3.0 mmol). The crude product was purified by column chromatography (silica, EtAc/hexane, 1:2; R_f=0.18).

Yield 1.53 g, 2 mmol, 67%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (m, 2H, CH_2), 1.65 (m, 4H, CH_2), 2.19 (quin, ^3J=7.2 Hz, 1H, CH_2COO), 2.30 (quin, ^3J=7.2 Hz, 1H, CH_2COO), 3.68 (m, 2H, CH_2N), 4.75 (d, ^2J=12 Hz, 1H, CH_2-Bn), 4.84 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.05 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.18 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.77 (d, ^3J=4 Hz, 1H, *CH), 5.87 (d, ^3J=4 Hz, 1H, *CH), 6.24 (br, 1H, NH), 7.04 (m, 6H, Ph), 7.27 (m, 6H, Ph), 7.40 (m, 5H, Ph), 7.92 (m, 6H, Ph), 8.40 (s, 1H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.2, 26.1, 19.2, 33.3, 39.7 (CH_2), 60.4, 67.7 (CH_2-Bn), 70.7, 71.1 (*CH), 115.7, 122.8, 124.0, 125.0, 125.4, 125.6, 126.6, 126.8, 127.7, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 128.9, 130.0, 131.0, 132.1, 133.7, 134.3, 134.7 (Ph, anthracene-Ph), 164.9, 165.5, 165.6, 169.48, 172.0 (C=O); MS (FAB): m/z (%): 752 (28) $[M+H]^+$, 661 (3) $[M-Bn]^+$, 205 (100) $[M-anthracene]^+$; $C_{46}H_{41}O_9N$ (751.3): calcd: C 73.49, H 5.50, N 1.86; found: C 73.84, H 5.56, N 2.29; UV/Vis (CH_2Cl_2) λ_{max} (ε) (nm): 384, 364, 347, 256 (124200).

4.5.22. Compound 25, dendron first generation (anthracene). Compound **25** was synthesized according to general procedure **III** with compound **10** (TFA-adduct) (416 mg; 0.63 mmol) and 9-anthracenecarboxylic acid (140 mg; 0.63 mmol). The crude product was purified by column chromatography (silica, EtAc/hexane, 1:2; R_f=0.18).

Yield 340 g, 0.45 mmol, 72%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (m, 2H, CH_2), 1.67 (m, 4H, CH_2), 2.20 (quin, ^3J=7.2 Hz, 1H, CH_2COO), 2.30 (quin, ^3J=7.2 Hz, 1H, CH_2COO), 3.69 (m, 2H, CH_2N), 4.77 (d, ^2J=12 Hz, 1H, CH_2-Bn), 4.85 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.07 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.19 (d, ^2J=12 Hz, 1H, CH_2-Bn), 5.77 (d, ^3J=4 Hz, 1H, *CH), 5.86 (d, ^3J=4 Hz, 1H, *CH), 6.22 (br, 1H, NH), 7.05 (m, 6H, Ph), 7.26 (m, 6H, Ph), 7.40 (m, 5H, Ph), 7.92 (m, 6H, Ph), 8.41 (s, 1H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 24.2, 26.1, 29.2, 33.3, 39.7 (CH_2), 60.4, 67.7 (CH_2-Bn), 70.7, 71.1 (*CH), 115.8, 124.0, 125.0, 125.4, 125.6, 126.6, 126.7, 127.7, 127.8, 127.9, 128.0, 128.2, 128.4, 128.5, 128.8, 128.9, 130.0, 131.0, 132.1, 133.7, 134.3, 134.7 (Ph, anthracene-Ph), 164.9, 165.5, 165.6, 169.48, 172.0 (C=O); MS (FAB): m/z (%): 1505 (4) $[2M+H]^+$, 752 (98) $[M+H]^+$, 661 (9) $[M-Bn]^+$, 205 (100) $[M-anthracene]^+$; $C_{46}H_{41}O_9N$ (751.3): calcd: C 73.49, H 5.50, N 1.86; found: C 73.14, H 5.83, N 1.56; UV/Vis (CH_2Cl_2) λ_{max} (ε) (nm): 384, 364, 347, 256 (124200).

4.5.23. Compound 26, dendron second generation (anthracene). Compound **26** was synthesized according to general procedure **III** with compound **16** (TFA adduct) (292 mg; 0.19 mmol) and with 9-anthracenecarboxylic acid (42 mg; 0.19 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 30:1; R_f=0.11).

Yield 210 mg, 0.13 mmol, 68%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (m, 20H, CH_2), 2.10 (m, 4H, CH_2COO), 2.43 (m, 1H, CH_2COO), 2.97 (m, 1H, CH_2COO), 3.15 (m, 6H, CH_2N), 4.60 (br, 1H, NH), 5.15 (m, 8H, CH_2-Bn), 5.80 (m, 6H, *CH), 6.24 (br, 1H, NH), 6.45 (br, 1H, NH), 7.28 (m, 36H, Ph), 7.92 (m, 8H, Ph), 8.40 (s, 1H, Ph-anthracene); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.9, 24.0, 24.2, 24.9, 25.5, 25.8, 25.9, 26.0, 28.7, 28.8, 28.9, 29.0, 29.1, 29.5 (CH_2), 33.0, 33.1, 33.7, 33.9 (CH_2COO), 38.9, 39.0, 39.2, 39.3, 39.5 (CH_2N),67.6, 67.7, 67.8, 67.9, (CH_2-Bn), 70.7, 70.8, 71.2, 71.7, 72.3, 72.7, (*CH), 125.1, 125.5, 126.7, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 129.0, 129.9, 130.1, 131.1, 132.2, 133.7, 133.9, 133.9, 134.5, 134.8, 134.9, 164.9, 165.1, 165.6, 165.7, 165.8, 165.9, 166.0, 166.1, 168.6, 169.3, 169.6, 171.9, 172.1, 172.2; MS (FAB): m/z (%): 1631 (12) $[M+H]^+$, 205 (100); $C_{94}H_{91}O_{23}N_3$ (1630.7): calcd: C 69.23, H 5.62, N 2.58; found: C 69.39, H 5.84, N 2.70; UV/Vis (CH_2Cl_2) λ_{max} (ε) (nm): 382, 362, 345, 330, 253 (124000).

4.5.24. Compound 27, dendron second generation (anthracene). Compound **27** was synthesized according to general procedure **III** with compound **17** (TFA adduct) (278 mg; 0.17 mmol) and with 9-anthracenecarboxylic acid (36 mg; 0.16 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 30:1; R_f=0.11).

Yield 190 mg, 0.12 mmol, 69%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (m, 20H, CH_2), 2.10 (m, 4H, CH_2COO), 2.42 (m, 1H, CH_2COO), 2.98 (m, 1H, CH_2COO), 3.15 (m, 6H, CH_2N), 4.60 (br, 1H, NH), 5.15 (m, 8H, CH_2-Bn), 5.80 (m, 6H, *CH), 6.26 (br, 1H, NH), 6.44 (br, 1H, NH), 7.28 (m, 36H, Ph), 7.92 (m, 8H, Ph), 8.40 (s, 1H, Ph-anthracene); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 23.9, 24.2, 24.9, 25.5, 25.8, 25.9, 28.7, 28.8, 29.0, 29.1, (CH_2), 33.0, 33.1, 33.7, 33.9 (CH_2COO), 38.9, 39.0, 39.5 (CH_2N),67.6, 67.7, 67.8, 67.9, (CH_2-Bn), 70.7, 71.1, 72.1, 72.3, 72.7, 73.3 (*CH), 125.1, 125.5, 126.7, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 129.0, 129.9, 130.1, 131.1, 132.2, 133.7, 133.8, 133.9, 134.5, 134.8, 134.9, 164.9, 165.1, 165.6, 165.7, 165.8, 165.9, 166.0, 166.1, 168.6, 169.3, 169.6, 171.9, 172.1, 172.2; MS (FAB): m/z (%): 1631 (10) $[M+H]^+$, 205 (100); $C_{94}H_{91}O_{23}N_3$ (1630.7): calcd: C 69.23, H 5.62, N 2.58; found: C 68.43, H 5.85, N 2.81; UV/Vis (CH_2Cl_2) λ_{max} (ε) (nm): 382, 362, 345, 330, 253 (124000).

4.5.25. Compound 28, dendron second generation (anthracene). Compound **28** was synthesized according to general procedure **III** with compound **18** (TFA adduct) (377 mg; 0.23 mmol) and with 9-anthracenecarboxylic acid (51 mg; 0.23 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 30:1; R_f=0.10).

Yield 220 mg, 0.13 mmol, 59%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 20H, CH_2), 2.10 (m, 4H, CH_2COO), 2.21 (m, 1H, CH_2COO), 2.98 (m, 1H, CH_2COO), 3.15 (m, 6H, CH_2N), 4.60 (br, 1H, NH), 5.15

(m, 8H, CH_2-Bn), 5.80 (m, 6H, *CH), 6.28 (br, 1H, NH), 6.58 (br, 1H, NH), 7.28 (m, 36H, Ph), 7.92 (m, 8H, Ph), 8.40 (s, 1H, Ph-anthracene); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.9, 24.0, 24.2, 24.9, 25.5, 25.8, 25.9, 26.0, 28.7, 28.8, 28.9, 29.0, 29.1, 29.5 (CH_2), 33.0, 33.1, 33.7, 33.9 (CH_2COO), 38.9, 39.0, 39.2, 39.3, 39.5 (CH_2N),67.6, 67.7, 67.8, 67.9, (CH_2-Bn), 70.7, 70.8, 71.2, 71.7, 72.3, 72.7, (*CH), 125.0, 125.5, 126.6, 127.9, 128.1, 128.2, 128.4, 128.5, 129.9, 131.1, 132.1, 133.6, 133.9, 134.4, 134.7, 164.9, 165.5, 165.6, 165.7, 165.9, 166.0, 168.6, 169.3, 169.6, 171.9, 172.0; MS (FAB): *m/z* (%): 1631 (14) $[M+H]^+$, 205 (100); $C_{94}H_{91}O_{23}N_3$ (1630.7): calcd: C 69.23, H 5.62, N 2.58; found: C 69.47, H 5.84, N 2.59; UV/Vis (CH_2Cl_2) λ_{max} (ε) (nm): 382, 362, 345, 330, 253 (124000).

4.5.26. Compound 29, dendron third generation (anthracene). Compound **29** was synthesized according to general procedure **III** with compound **19** (TFA adduct) (130 mg; 0.04 mmol) and with 9-anthracenecarboxylic acid (8 mg; 0.04 mmol). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 15:1; R_f=0.19).

Yield 64 mg, 0.019 mmol, 22%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 20H, CH_2), 2.15 (m, 14H, CH_2COO), 3.15 (m, 14H, CH_2N), 4.60 (br, 1H, NH), 5.15 (m, 16H, CH_2-Bn), 5.80 (m, 14H, *CH), 6.45 (br, 6H, NH), 7.28 (m, 72H, Ph), 7.92 (m, 16H, Ph), 8.40 (s, 1H, Ph-anthracene); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 24.0, 24.9, 25.6, 25.8, 25.9, 26.1, 28.1, 28.8, 29.0, 29.1, 31.7, 32.0, 33.0, 33.1, 33.5, 33.9, 35.2, 36.9, 39.1, 39.2, 39.3, 39.7, 49.1, 50.3, 53.7, 54.7, 67.7, 67.8, 67.9, 70.7, 71.2, 72.1, 72.3, 72.4, 72.9, 125.0, 125.5, 126.6, 127.9, 128.3, 128.4, 128.6, 129.9, 130.0, 133.6, 133.9, 134.4, 134.5, 142.0, 156.6, 165.0, 165.5, 165.7, 166.0, 166.2, 166.0, 171.9, 172.1; MS (FAB): *m/z* (%): 3390 (5) $[M+H]^+$, 3185 $[M-\text{anthracene}]^+$ (100); $C_{190}H1_{91}O_{51}N_7$ (3388.6): calcd: C 67.35, H 5.68, N 2.89; found: C 67.49, H 5.38, N 2.80; UV/Vis (CH_2Cl_2) λ_{max} (ε) (nm): 383, 362, 345, 330, 254 (125000).

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