FULL PAPER

Stilbenoid Dendrimers

Herbert Meier,*[a] Matthias Lehmann,[a] and Ute Kolb[b]

Abstract: The first five generations of the stilbenoid dendrimers 1^n ($n = 1–5$) have been prepared by a combined coupled synthesis (between the generations of the dendrons **8 – 12**) and convergent synthesis. Wittig – Horner reactions together with a protecting group technique yield monodisperse compounds of high constitutional and configurational purity. The solubility of the stiff molecules, which have primarily a disklike shape in the first and second generations and a cylindrical shape in the third, fourth, and fifth generations, is governed by the alkoxy chains that are attached to the peripheral benzene rings. The number of stilbene building blocks increases according to the formula $3(2^n - 1)$ from 3 in the first generation ($n = 1$) to 93 in the fifth generation ($n = 5$). Consequently, the molecular mass reaches 24000 in 1^5**b** which contains 144 hexyloxy chains. An exact measurement of the mass is provided by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. In solution, the stilbenoid dendrimers 1^n exhibit a strong tendency to aggregate, which increases from generation to generation. In the pure state, columnar mesophases Col_{hd} (**1^1b**, **1^1c**, **1^2b**, and **1^2c**) and Col_{ob} (**1^2b**, **1^2c**) are formed; intramolecular steric hindrance prevents such ordered arrangements in higher generations 1^n ($n = 3, 4, 5$).
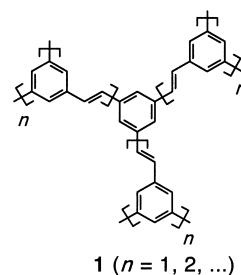
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Introduction

Stilbenoid compounds exhibit interesting photochemical and photophysical properties and are suitable for various applications in materials science.[1] Apart from their commercial use as optical brighteners and laser dyes, their application in light-emitting diodes (LED), photoresists, photoconductive devices, imaging and optical switching techniques and materials for nonlinear optics (NLO) are being investigated on this molecular basis.[1, 2, 3, 4, 5]

Another structural principle of high actuality is represented by dendrimers.[6, 7, 8, 9, 10] Therefore, the obvious idea was to combine both principles and design dendrimers **1** which consist of stilbene building blocks.

We conceived a combined coupled synthesis (between the different generations) and convergent synthesis in order to obtain constitutionally and configurationally pure compounds. Recently, we reported briefly on the first three

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1 (*n* = 1, 2, ...)

generations of such highly symmetrical systems.[11] At the same time, less symmetrical stilbenoid dendrimers were prepared by L. Yu and co-workers.[12] With regards to the rigidity and the absence of saturated carbon atoms in the skeletons, these dendrimers are related to the tolane dendrimers that were first obtained by J. S. Moore and co-workers.[13, 14]

Rigid hydrocarbons often have a very low solubility; therefore, we decided to attach alkoxy chains onto the periphery of the dendrimers **1**. Furthermore, long flexible side chains are a precondition for the formation of liquid crystalline phases. Table 1 gives a survey of our dendrimers that contain peripheral trihexyloxy-substituted benzene rings.

As a consequence of the "dendritic tree", the number of olefinic double bonds as well as the number of alkoxy chains grows strongly from generation to generation. The molecular mass already reaches 24000 in the fifth generation.

Table 1. Stilbenoid dendrimers 1^n.

Genera-tion	Stilbene units (number of olefinic double bonds)	Hydrocarbon skeletons	Compounds with 3,4,5-tri-hexyloxy-substituted peripheral benzene rings	
			formula	molecular mass
n	$3(2^n-1)$	$C_{24\cdot2^n-18}H_{18\cdot2^n-12}$	$C_{51\cdot2^n-18}H_{72\cdot2^n-12}O_{9\cdot2^n-1}$	m
1	3	$C_{30}H_{24}$	$C_{84}H_{132}O_9$	1286
2	9	$C_{78}H_{60}$	$C_{186}H_{276}O_{18}$	2800
3	21	$C_{174}H_{132}$	$C_{390}H_{564}O_{36}$	5829
4	45	$C_{366}H_{276}$	$C_{798}H_{1140}O_{72}$	11886
5	93	$C_{750}H_{564}$	$C_{1614}H_{2292}O_{144}$	24000

Results and Discussion

Synthesis: The convergent synthesis of the dendrimers **1** consisted of the separate preparation of the core and the dendrons which were then linked together in the final reaction step. The component for the core was the threefold phosphonic ester **3** that was obtained by an Arbusov rearrangement from 1,3,5-tris(bromomethyl)benzene (**2**) and triethyl phosphite (Scheme 1).
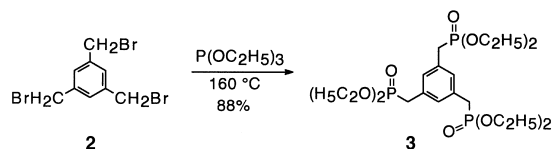
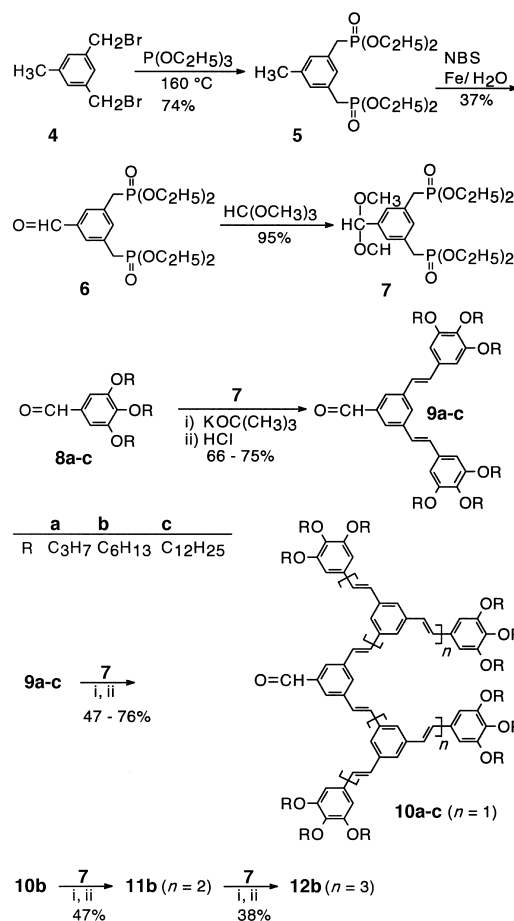

Scheme 1. Preparation of the core.

When bis(bromomethyl)toluene (**4**) was used instead of **2**, the diphophonate **5** was obtained, which was subsequently oxidized to the aldehyde **6** (Scheme 2). The protection of the formyl group as acetal **7** prevented self-condensation, so that a Wittig–Horner reaction between **7** and the aldehydes **8a–c** gave the higher aldehydes **9a–c**. The deprotection of the formyl group occurred during the work-up of this step. The same procedure was then used for the further extension of the aldehyde components which represented the dendrons. Thus, **9a–c** was transformed to **10a–c**, **10b** to **11b** and finally **11b** to **12b**. The diphosphonate **7** served as the extension and branching unit for the generation of the next higher dendron in each of the steps **8 → 9 → 10 → 11 → 12**; therefore, we regard the process for the formation of the dendritic generations to be a coupled synthesis.

The last reaction step in the formation of the dendrimers **1** consisted of a threefold Wittig–Horner reaction between the core **3** and the dendrons **8–12** (Scheme 3). The purified dendrons did not contain any *cis*-configured double bonds and the *trans* stereoselectivity of the final step is so high that there were no indications of any *cis*-configured double bonds in the dendrimers either.

The yields of **1** decreased as the steric hindrance increased. Since the hexyloxy substituents gave the best results in the third generation, we continued with these side chains in the fourth and fifth generation. The reactive centers in the condensation reactions **3 + 11b** and **3 + 12b** are so strongly sterically shielded, that the reaction times became very long, namely 10 and 18 days, respectively. Evidently, the process
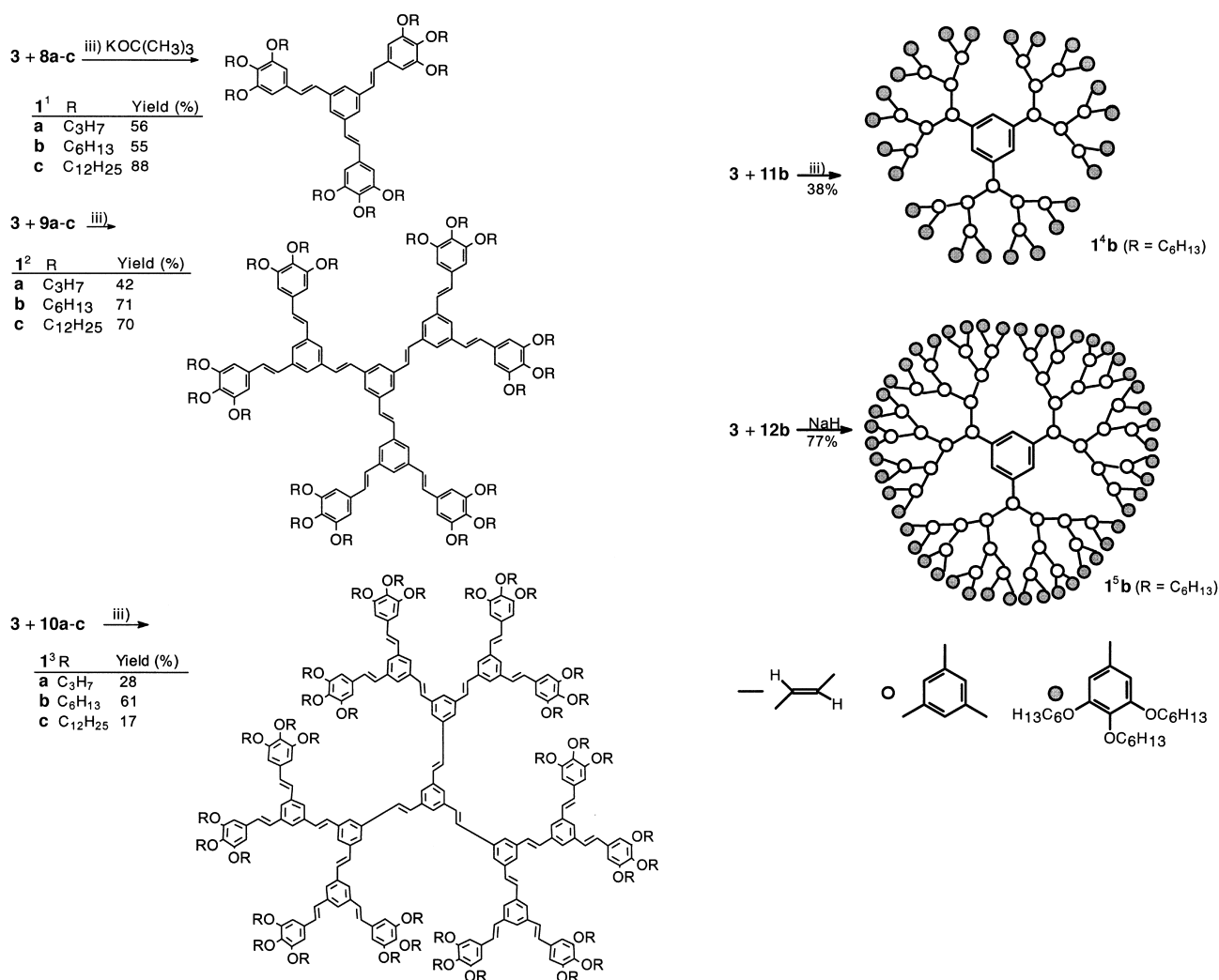

Scheme 2. Preparation of the dendrons.

reaches its limits with the fifth generation. We had to use NaH instead of *t*BuOK for the preparation of **1⁵b**; an increase of the temperature to above 30 °C did not prove to be favorable.

Spectroscopic characterization: Supplementary to the FD method, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometrical techniques proved to be very useful for the identification of the higher dendrimers of **1**; in particular, we were able to see whether the threefold condensation in the final step was complete or not. The results obtained for 1^n ($n = 1–5$) are given in Table 2. The first four generations 1^n were obtained in high purity; the compound **1⁵b** contains solvent molecules which are located in the cavities of the dendritic cylinder.[15, 16]

The ^{1}H NMR spectra of **1¹a–1¹c** in CDCl₃ are highly resolved. The protons of the core exhibit singlet signals at $\delta = 7.50 \pm 0.01$, while the protons of the peripheral rings give singlets at $\delta = 6.73 \pm 0.01$. The olefinic protons give rise to an AB pattern at $\delta = 6.98 \pm 0.01$ and 7.08 ± 0.02, whereby the resonance at higher field corresponds to the protons which are closer to the core (NOE measurements). The coupling constants amount to 16.2 ± 0.2 Hz. The spectra of **1²a–1²c** in CDCl₃ gave similar results; however, only broadened ^{1}H NMR signals could be obtained for the higher generations. This effect is caused by the aggregation[17] which is discussed below.

The ^{13}C NMR data are listed in the Experimental Section. The most interesting band in the FT-IR spectra of 1^n

3 + 8a-c $\xrightarrow{\text{iii) KOC(CH}_3)_3}$

$\mathbf{1^1}$	R	Yield (%)
a	C_3H_7	56
b	C_6H_{13}	55
c	$C_{12}H_{25}$	88

3 + 9a-c $\xrightarrow{\text{iii}}$

$\mathbf{1^2}$	R	Yield (%)
a	C_3H_7	42
b	C_6H_{13}	71
c	$C_{12}H_{25}$	70

3 + 10a-c $\xrightarrow{\text{iii}}$

$\mathbf{1^3}$	R	Yield (%)
a	C_3H_7	28
b	C_6H_{13}	61
c	$C_{12}H_{25}$	17

3 + 11b $\xrightarrow[38\%]{\text{iii}}$ $\mathbf{1^4b}$ (R = C_6H_{13})

3 + 12b $\xrightarrow[77\%]{\text{NaH}}$ $\mathbf{1^5b}$ (R = C_6H_{13})

Scheme 3. Preparation of the dendrimers $\mathbf{1^n}$ ($n = 1-5$).[15]

Table 2. Mass spectrometry of the dendrimers $\mathbf{1^n}$ ($n = 1-5$).

Compound	Method[a]	Peak group maxima		
		species	found	calculated
$\mathbf{1^1a}$	A	$[M+H]^+$	907.6	907.6
$\mathbf{1^1b}$	A	$[M+H]^+$	1286.1	1286.0
$\mathbf{1^1c}$	A	$[M^{+\cdot}]$	2043.0	2042.8
$\mathbf{1^2a}$	A	$[M^{+\cdot}]$	2042.2	2042.2
$\mathbf{1^2b}$	B	$[M+Ag]^+$	2908.6	2908.0
$\mathbf{1^2c}$	C	$[M^{+\cdot}]$	4315.7	4314.7
$\mathbf{1^3a}$	C	$[M^{+\cdot}]$	4314.1	4313.5
$\mathbf{1^3b}$	B	$[M+Ag]^+$	5936.1	5936.1
$\mathbf{1^3c}$	C	$[M^{+\cdot}]$	8859.6	8858.6
$\mathbf{1^4b}$	B	$[M+Ag]^+$	11993	11993.4
$\mathbf{1^5b}$	B	$[M+Ag+2\,C_7H_8]^+$	24290[16]	24291.2

[a] A = Field desorption; B = MALDI-TOF in a matrix of 1,8,9-trihydrox-yanthracene (dithranol) in the presence of CF_3CO_2Ag; C = as B but without Ag^+ ions.

($n = 1-5$) is the wagging vibration of the *trans*-configured double bonds which is located at 955 ± 5 cm^{-1}.

Molecular shape: The first generation $\mathbf{1^1a} - \mathbf{1^1c}$ are totally planar molecules. A X-ray crystal structure analysis of $\mathbf{1^1a}$[18] showed that the torsional angles in the stilbenoid skeleton are,

at most, $\pm 6°$; of course, the side chains can be twisted out of the molecular plane. The free or dissolved molecule $\mathbf{1^1a}$ has a D_{3h} symmetry with fast flips of the outer benzene rings.

In order to get an idea of the shape of the higher generations, we developed molecular models of the compounds $\mathbf{1^nb}$ ($n = 1-5$) with the CERIUS 2.0 software. Because of the complexity and the size of the higher dendrimers, a full geometrical optimization was not possible; thus, we had to make some simplifying assumptions:

1) all bond lengths and bond angles correspond to standard values;
2) we assumed C_3 symmetry for the central tristyrylbenzene moiety and C_2 symmetry for the remainder dendrons;
3) interaction of the hexyloxy chains was neglected, the chains were directed in an all-*trans* conformation radially away from the peripheral benzene rings;
4) the torsions around the single bonds were driven until acceptable distances (340 – 450 pm) between the aromatic units were reached.

The models revealed that molecule $\mathbf{1^2b}$ is still a flat disk; however, from the third generation onwards the crowding gets so severe that the steric repulsions force an extension into the "third dimension". Thus the disklike shape is transformed into

a cylindrical shape. This effect is illustrated by the structures of the third and the fifth generations in Figure 1 and Figure 2, respectively.
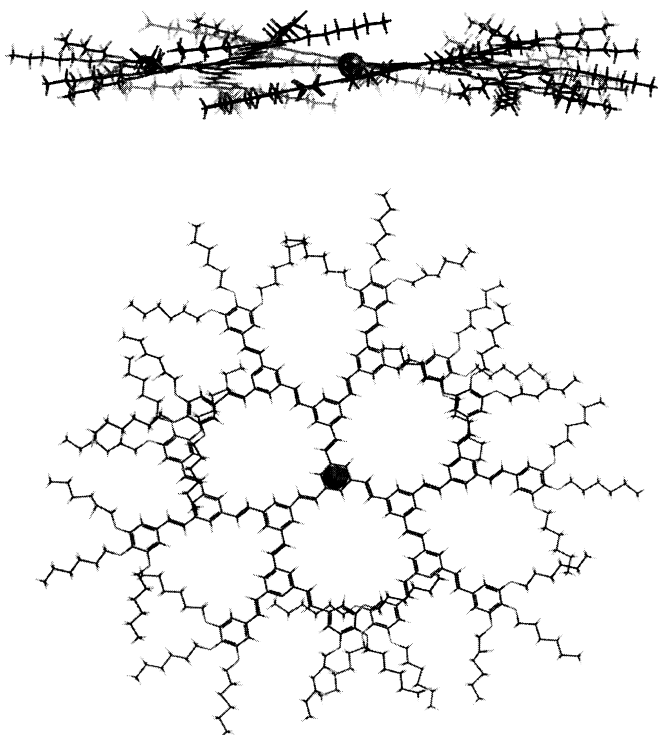

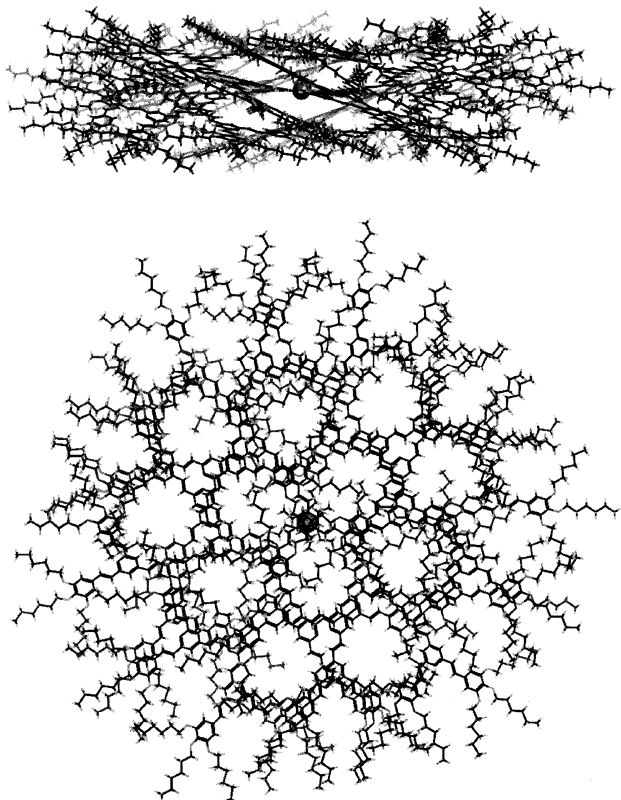Figure 1. Model of the third generation 1^3b. View from the side and from above.

Figure 2. Model of the fifth generation 1^5b. View from the side and from above.

In addition, it can be seen from these model structures that there is a series of cavities around the core in which guest molecules can be incorporated.[19] The dependence of the diameter (Θ) and the height (h) of the disks/cylinders on the generation n is shown in Figure 3. The diameter Θ increases as
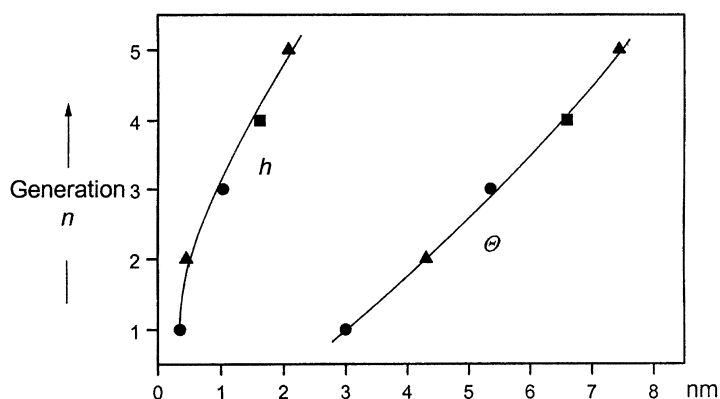
Figure 3. Diameter (Θ) and height (h) of the disks/cylinders of 1^nb as a function of the generation n.

n increases; however the growth is less than linear. Experimental proof for the size of these nanoparticles is attempted by electron microscopy. GPC experiments gave some good indications of the size: within the series of dendrimers 1^nb, the retention time (t) should be an exponential function of the diameter Θ [Eq. (1)].[20] The plot of t against Θ is given in Figure 4:

$$t = t_O + t_i e^{\left(\frac{\Delta G_P}{kT} + \frac{s\Theta}{2}\right)}$$ (1)

where $t_O = 16.63 \pm 0.49$ min   retention time corresponding to the total volume of the mobile phase

$t_i = 5.37 \pm 0.47$ min   retention time corresponding to the volume of the stationary phase

$e^{\frac{\Delta G_P}{kT}} = e^{-0.97 \pm 0.17}$ distribution coefficient for the substrate–sorbent interaction

$s = 0.66 \pm 0.11$ nm^{-1} surface area per unit pore volume

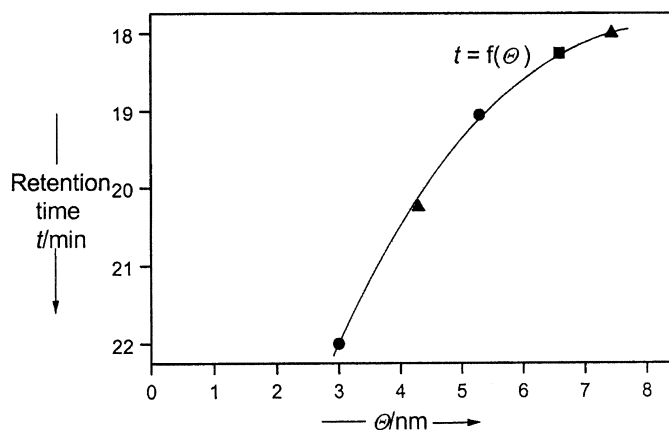The good-fit parameter ($\chi^2 = 0.012$) demonstrates the consistency of the Θ values within the series.

Figure 4. GPC retention times t as a function of the molecular diameter Θ.

Supramolecular properties: The above discussion of the ^{1}H NMR spectra already revealed that the dendrimers 1^n exhibit a tendency to aggregate which increases with increasing n.[11] Apolar solvents, such as cyclohexane or toluene, are particularly suitable for the formation of such aggregates; chloroform is less suitable because it strongly interacts with the electron-rich peripheral benzene rings. The temperature dependency of the aggregation has already been reported in a previous short paper.[11] Altogether, there are three factors which are involved in the broadening of the ^{1}H NMR signals: 1) the exchange of molecules between aggregates, 2) the reduced mobility of the single molecules in the aggregates, and 3) the reduced mobility of molecular segments.

The latter can be judged by the relaxation times T_1 of the carbon atoms. This was investigated with the model compound $1^1\mathbf{d}$ (Figure 5):[18] T_1 decreased significantly from the periphery to the center, which means that the mobility decreased in the same direction. Restricted mobility in the center favors aggregation which subsequently reduces the mobility even further.
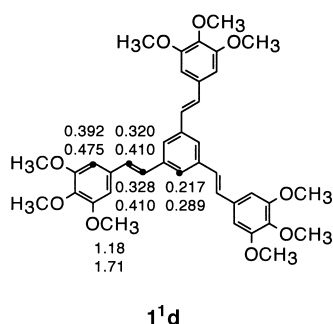
Figure 5. Longitudinal relaxation times T_1 of the tertiary carbon atoms of compound $1^1\mathbf{d}$ in CDCl$_3$. The upper values (in seconds) correspond to 293 K, the lower values to 310 K.

In principle, the same behavior can be assumed for the higher generations. The larger the interior part of restricted mobility is, the higher the tendency of aggregation should be.

In addition to the interaction of the stilbenoid skeletons, the alkoxy side chains should also contribute to the aggregation. This point is particularly important for aggregation in the pure state, namely, for the formation of mesophases, where a microphase segregation between the stilbenoid skeletons and the surrounding alkoxy chains could occur. Propoxy chains are not long enough for the formation of liquid crystals. The compounds of the first and second generations with hexyloxy or dodecyloxy chains form columnar liquid crystalline phases; the steric crowding in the higher generations does not permit a regular arrangement. The results of differential scanning calorimetry (DSC) investigations of compounds $1^n\mathbf{a-c}$ are given in Table 3.

The higher generations ($n = 3, 4, 5$) of the compounds $1^n\mathbf{a-c}$ are oils or they form glassy or solid states, which are directly transformed to isotropic phases on heating.

A detailed discussion of the characterization of the LC phases by temperature-dependent small-angle scanning X-ray measurements will be given elsewhere. In the context of this paper, the cell parameters are of interest because they can be

Table 3. DSC measurements of the compounds $1^n\mathbf{a-c}$.

Compound[a]	Phase transitions[b]						$T/\Delta H$
$1^1\mathbf{a}$	H Cr				189/45		I
	C Cr	←			175/-44		I
$1^1\mathbf{b}$	H g		-15 (T_g) →	Col$_{hd}$		74/4 →	I
	C g	←	-18 (T_g)	Col$_{hd}$	←	71/-4	I
$1^1\mathbf{c}$	H Cr$_1$	13/49 →	Cr$_2$ 19/-21 →	Cr$_3$ [21] 38/39 →	Col$_{hd}$	75/10 →	I
	C Cr$_1$	←	8/-61	Col$_{hd}$	←	74/-10	I
$1^2\mathbf{a}$	H Cr				161/20		I
	C Cr	←			154/-11		I
$1^2\mathbf{b}$	H Col$_{hd}$		[c] →	Col$_{ob}$		144/8 →	I
	C Col$_{hd}$ ←		[c]	Col$_{ob}$	←	142/-7	I
$1^2\mathbf{c}$	H Cr	11/59 →	Col$_{hd}$	32/4 →	Col$_{ob}$	99/17 →	I
	C Cr	←	5/-48 →	Col$_{ob}$	←	91/-17	I

[a] Compound $1^3\mathbf{a}$ is a solid that melts at 142 °C, $1^3\mathbf{b}$ is a glass with T_g of −45 °C. $1^3\mathbf{c}$, $1^4\mathbf{b}$ and $1^5\mathbf{b}$ are oils. [b] Cr: crystalline phase; g: glassy phase; Col$_{hd}$: columnar hexagonal disordered phase; Col$_{ob}$: columnar oblique phase; I: isotropic phase. Measurement of the second heating process H and the first cooling process C: Phase transition temperatures (onset) T [°C]/transition enthalpies ΔH [kJ mol^{-1}]. [c] Phase transition only visible in the X-ray small-angle scattering. Presumably the ΔH value for this transition is very small.

compared to the disc parameters of the models. The Col$_{hd}$ phases of $1^1\mathbf{b}$ and $1^2\mathbf{b}$ have hexagonal unit cells of 2.74 and 3.69 nm, respectively. These values are somewhat smaller than the model values Θ (Figure 3). The packing of the peripheral hexyloxy chains is important for the generation of the mesophases; however, the chains are probably less radially stretched than in the models.

Conclusions

The dendrimers 1^n ($n = 1 - 5$), which consist of *trans*-stilbene building blocks, can be prepared in a constitutionally and configurationally pure form by application of the Wittig–Horner reaction combined with a protecting group technique. The final reaction step of the convergent synthesis is the most difficult step because the attachment of the three dendrons to the core is impeded by steric hindrance, which increases from generation to generation. Thus, this synthetic strategy seems to come to an end at the fifth generation; although dendrons of higher generations might be easily acceptable by the iterative process shown in Scheme 2.

The first two generations, 1^1 and 1^2, have a disklike shape and form columnar liquid crystalline phases, provided that hexyloxy or dodecyloxy side chains are attached to the periphery; propoxy chains are to short to permit such an intermolecular stacking.

In contrast to the planar systems 1^1 and 1^2, the higher generations 1^3, 1^4 and 1^5, assume a cylindrical shape. The height and the diameter (Θ) of the cylinders, obtained by model studies, correlate reasonably with GPC data.

Based on photophysical and photochemical properties of stilbene systems, the compounds **1** promise interesting applications in materials science. A particular feature of these stiff dendrimers is the existence of cavities close to the core in which guest molecules, for example triplet sensitizers, can be incorporated.[19]

Experimental Section

General methods: Melting points were determined on a Büchi melting point apparatus and are uncorrected. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC 7 instrument. IR spectra were obtained on a Beckman Acculab 4 in KBr pellets or in neat form. PFT ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ with Bruker AM 400, AC 200 and ARX 400 spectrometers. Mass spectra were obtained on Varian MAT CH 7A (EI-MS), Finnigan MAT 95 (FD-MS) and Bruker Reflex (MALDI-TOF) spectrometers. The X-ray diffraction was measured with a Siemens D 500 diffractometer (Cu$_{K\alpha}$ radiation; $\lambda = 1.54189$ Å). The GPC measurements were obtained with a Waters 510/Waters 410/Waters 486 PSS column arrangement.

Hexaethyl 1,3,5-benzenetriyltris(methylenephosphonate) (3): Starting from 1,3,5-tris(bromomethyl)benzene (**2**) and triethyl phosphite, the preparation was performed according to a procedure described in the literature.[22] Yield: 88%, viscous oil; ^{1}H NMR (CDCl$_3$): $\delta = 1.13$ (t, 18 H; CH$_3$), 2.99 (d, 6 H; PCH$_2$), 3.89 (m, 12 H; OCH$_2$), 7.01 (s, 3 H; aromat. H); ^{13}C NMR (CDCl$_3$): $\delta = 16.1$ (CH$_3$), 32.2 (PCH$_2$, $^1J = 137.0$ Hz), 61.9 (OCH$_2$, 129.6 (aromat. CH), 132.0 (aromat. C$_q$).

Tetraethyl 5-methyl-1,3-phenylenebis(methylenephosphonate) (5): The preparation was performed analogously to **2 → 3** from 1,3-bis(bromomethyl)-5-methylbenzene (**4**) and triethyl phosphite. Yield: 74%; colorless oil; b.p. 218 °C (0.1 Torr); ^{1}H NMR (CDCl$_3$): $\delta = 1.12$ (t, 12 H; CH$_3$), 2.17 (s, 3 H; 5 CH$_3$), 2.95 (d, 4 H; PCH$_2$), 3.88 (m, 8 H; OCH$_2$), 6.88 ("s", 3 H; aromat. H); ^{13}C NMR (CDCl$_3$): $\delta = 16.2$ (CH$_3$), 21.1 (5 CH$_3$), 33.4 (PCH$_2$), 61.9 (OCH$_2$), 128.2 (C2), 129.1 (C4, C6), 131.6 (C1, C3), 138.1 (C5): EI MS (70 eV): m/z (%): 392 (79, [$M^{+\cdot}$]), 256 (100), 119 (48); elemental analysis: calcd for C$_{17}$H$_{30}$O$_6$P$_2$: C 52.04, H 7.71; found C 52.01, H 7.69.

Tetraethyl 5-formyl-1,3-phenylenebis(methylenephosphonate) (6): Compound **5** (10.4 g, 26.5 mmol), N-bromosuccinimide (NBS) (10.0 g, 56.2 mmol), and azobisisobutyronitrile (AIBN) (100 mg, 0.6 mmol) were stirred in dry CCl$_4$ (160 mL) and refluxed for 4 h. The filtered solution was washed with saturated NaHCO$_3$ solution (50 mL) and water (50 mL) and dried over MgSO$_4$. Volatiles were removed and the oily residue treated with water (100 mL) and iron powder (0.12 g, 2.14 mmol). The mixture was refluxed for 4 h, and the aqueous layer then neutralized with NaHCO$_3$ and extracted three times with CHCl$_3$. The solution was dried over MgSO$_4$ and evaporated. The residue was dissolved in diethyl ether (400 mL) and extracted with half concentrated NaHSO$_3$. The aqueous phase was extracted with diethyl ether (200 mL) and treated with HCl (37%, 40 mL) and CHCl$_3$ (400 mL). After the mixture had been stirred for 3 h, the organic layer was separated and the aqueous layer extracted with CHCl$_3$ until the aldehyde was no longer present (checked with 2,4-dinitrophenylhydrazine). The combined organic layers were neutralized and dried over MgSO$_4$. Evaporation yielded 3.92 g (37%) of a yellowish oil. ^{1}H NMR (CDCl$_3$): $\delta = 1.14$ (t, 12 H; CH$_3$), 3.10 (d, 4 H; PCH$_2$), 3.93 (m, 8 H; OCH$_2$), 7.41 (m, 1 H, 2 H), 7.60 (m, 2 H, 4 H, 6 H), 9.87 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 16.1$ (CH$_3$), 33.1 (PCH$_2$), 62.0 (OCH$_2$), 129.3 (C4, C6), 133.2 (C2), 136.8 (C1, C3), 136.8 (C5), 191.6 (CHO); EI MS (70 eV): m/z (%): 406 (65, [$M^{+\cdot}$]), 270 (100), 133 (29); elemental analysis: calcd for C$_{17}$H$_{28}$O$_7$P$_2$: C 50.25, H 6.95; found C 50.61, H 7.25.

Tetraethyl 5-dimethoxymethyl-1,3-phenylenebis(methylenephosphonate) (7): Compound **6** (1.96 g, 4.8 mmol), trimethyl orthoformate (5 mL, 4.46 g, 30.1 mmol), and DOWEX 50W-X8 (1.2 g) were refluxed in dry methanol (30 mL) overnight.[23] After treatment with Na$_2$CO$_3$ (1.2 g, 11.3 mmol), the solution was filtered and the solvent removed. The oily residue was extracted with acetone (50 mL). Evaporation of the acetone solution yielded 2.06 g (95%) of a viscous, almost colorless oil. ^{1}H NMR (CDCl$_3$): $\delta = 1.19$ (t, 12 H; CH$_3$), 3.09 (d, 4 H; PCH$_2$), 3.25 (s, 6 H; OCH$_3$), 3.95 (m, 8 H; OCH$_2$), 5.31 (s, 1 H; 5 CH), 7.16 ("s", 1 H, 2 H), 7.23 (m, 2 H,

4 H, 6 H); ^{13}C NMR (CDCl$_3$): $\delta = 16.3$ (CH$_3$), 33.6 (PCH$_2$), 52.6 (OCH$_3$), 62.1 (OCH$_2$), 102.7 (5 CH), 126.8 (C4, C6), 131.2 (C2), 132.0 (C1, C3), 138.7 (C5); EI MS (70 eV): m/z (%): 452 (1, [$M^{+\cdot}$]), 421 (100), 315 (18); elemental analysis: calcd for C$_{19}$H$_{34}$O$_8$P$_2$: C 50.44, H 7.57; found C 49.99, H 7.53.

(E,E)-3,5-Bis[2-(3,4,5-tripropoxyphenyl)ethenyl]benzaldehyde (9a): Compound **7** (2.4 g, 5.4 mmol) and 3,4,5-tripropoxybenzaldehyde (**8a**, 3.1 g, 11.0 mmol) were dissolved in THF (15 mL) and added dropwise to KOC(CH$_3$)$_3$ (2.0 g, 18.0 mmol) in THF (50 mL). After stirring at room temperature for 12 h, the mixture was poured onto crushed ice (100 g). Addition of 2 M HCl (50 mL) and CHCl$_3$ (50 mL) led to the cleavage of the acetal. After 12 h at ambient temperature, the product (dissolved in CHCl$_3$) was precipitated by addition of ethanol. Yield: 2.4 g (67%), yellowish needles; m.p. 153 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.06$ (m, 18 H; CH$_3$), 1.83 (m, 12 H; CH$_2$), 3.95/3.99 (2t, 12 H; OCH$_2$), 6.73 (s, 4 H; aromat. H), 6.99 (d, $^3J = 16.1$ Hz, 2 H; olefin. H[24]) 7.14 (d, $^3J = 16.1$ Hz, 2 H; olefin. H) 7.80 ("s", 1 H, 4 H), 7.85 ("s", 2 H, 2 H, 6 H), 10.03 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 10.6$ (CH$_3$), 22.8, 23.5 (CH$_2$), 70.8, 75.2 (OCH$_2$), 105.5 (aromat. CH), 126.0 (C2, C6 and inner olefin. CH), 129.9 (C4), 130.9 (outer olefin. CH), 131.9 (aromat. C$_q$), 137.3 (C1), 138.8 (C3, C5 and C$_q$O), 153.4 (C$_q$O), 192.3 (CHO); FD MS: m/z (%): 658 (100, [$M^{+\cdot}$]); elemental analysis: calcd for C$_{41}$H$_{54}$O$_7$: C 74.74, H 8.26; found 74.76, H 8.22.

(E,E)-3,5-Bis[2-(3,4,5-trihexyloxyphenyl)ethenyl]benzaldehyde (9b): Preparation analogous to **9a**. Yield: 66% of a waxy compound with a clearing point at 53 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.90$ (m, 18 H; CH$_3$), 1.20–1.60 (m, 36 H; CH$_2$), 1.78 (m, 12 H; CH$_2$), 3.97, 4.01 (2t, 12 H; OCH$_2$), 6.73 (s, 4 H; aromat. H), 7.00 (d, $^3J = 16.3$ Hz, 2 H; inner olefin. H), 7.14 (d, $^3J = 16.3$ Hz, 2 H; outer olefin. H), 7.80 ("s", 1 H, 4 H), 7.85 ("s", 2 H, 2 H, 6 H), 10.04 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 14.1$ (CH$_3$), 22.3–31.8 (CH$_2$) 69.3, 73.6 (OCH$_2$), 105.4 (aromat. CH), 126.0 (C2, C6 and inner olefin. CH), 129.9 (C4), 130.9 (outer olefin. CH), 131.8 (aromat. C$_q$), 137.2 (C1), 138.8 (C3, C5 and C$_q$O) 153.4 (C$_q$O), 192.3 (CHO); FD MS: m/z (%): 911 (100, [$M^{+\cdot}$]); elemental analysis: calcd for C$_{59}$H$_{90}$O$_7$: C 77.76, H 9.95; found C 77.39, H 9.80.

(E,E)-3,5-Bis-(3,4,5-tridodecyloxyphenyl)ethenyl]benzaldehyde (9c): Preparation analogous to **9a**. Yield 75% of a waxy solid with a clearing point at 57 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.86$ (m, 18 H; CH$_3$), 1.40–1.85 (m, 120 H; CH$_2$), 3.98, 4.01 (2t, 12 H; OCH$_2$), 6.72 (s, 4 H; aromat. H), 7.00 (d, $^3J = 16.2$ Hz, 2 H; inner olefin. H), 7.13 (d, $^3J = 16.3$ Hz, 2 H; outer olefin. H), 7.80 ("s", 1 H, 4 H), 7.85 ("s", 2 H, 2 H, 6 H), 10.04 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.1–31.9 (CH$_2$), 69.4 (OCH$_2$), 73.6 (OCH$_2$), 105.8 (aromat. CH), 126.0, 126.1 (C2, C6 and inner olefin CH), 129.9 (C4), 131.0 (outer olefin. CH), 131.9 (aromat. C$_q$), 137.4 (C1), 138.9, 139.1 (C3, C5 and C$_q$O), 153.5 (C$_q$O), 192.1 (CHO); FD MS: m/z (%): 1416 (100, [$M^{+\cdot}$]); elemental analysis: calcd for C$_{95}$H$_{162}$O$_7$: C 80.56, H 11.53; found C 80.55, H 11.48.

(E,E,E,E,E)-3,5-Bis{2-[3,5-bis[2-(3,4,5-tripropoxyphenyl)ethenyl]phenyl]ethenyl}benzaldehyde (10a): The preparation was performed as described for **9a**. After 1 h at room temperature the reaction mixture was refluxed for 2 h. Yield: 47%; light yellow crystals; m.p. 183 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.05$ (m, 36 H; CH$_3$), 1.78, 1.85 (2 m, 24 H; CH$_2$), 3.96, 3.99 (2t, 24 H; OCH$_2$), 6.74 (s, 8 H; aromat. H), 6.99 (d, $^3J = 16.2$ Hz, 4 H; olefin. H), 7.09 (d, $^3J = 16.2$ Hz, 4 H; olefin. H), 7.21, 7.26 (2 d, $^3J = 16.2$ Hz, 4 H; olefin. H), 7.53 ("s", 6 H; aromat. H), 7.86 ("s", 1 H, 4 H), 7.91 ("s", 2 H, 2 H, 6 H), 10.06 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 10.5$, 10.6 (CH$_3$), 22.8, 23.5 (CH$_2$), 70.9, 75.2 (OCH$_2$), 105.6 (aromat. CH), 123.8, 124.3, 126.5, 130.1 (aromat. CH), 127.2, 127.6, 129.7, 130.6 (olefin. CH), 132.3, 137.4, 137.4, 138.3, 138.8, 138.8 (aromat. C$_q$, C$_q$O), 153.4 (C$_q$O), 192.0 (CHO); FD MS: m/z (%): = 1417 (100, [M+H]$^+$); elemental analysis: calcd for C$_{91}$H$_{114}$O$_{13}$: C 77.19, H 8.12; found C 77.37, H 8.06.

(E,E,E,E,E)-3,5-Bis{2-[3,5-bis[2-(3,4,5-trihexyloxyphenyl)ethenyl]phenyl]ethenyl} benzaldehyde (10b): The preparation was performed as described for **10a**. Yield: 72%; light yellow, waxy solid with a clearing point of 115 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.90$ (m, 36 H; CH$_3$), 1.34, 1.48 (2 m, 108 H; CH$_2$), 1.75, 1.82 (2 m, 24 H; CH$_2$), 3.97, 4.03 (2t, 24 H; OCH$_2$), 6.74 (s, 8 H; aromat. H), 7.01 (d, $^3J = 16.2$ Hz, 4 H; olefin. H), 7.11 (d, $^3J = 16.3$ Hz, 4 H; olefin. H), 7.24 (d, $^3J = 16.3$ Hz, 2 H; olefin. H), 7.29 (d, $^3J = 16.3$ Hz, 2 H; olefin. H), 7.55 ("s", 4 H; aromat. H), 7.57 ("s", 2 H; aromat. H), 7.88 ("s", 1 H, 4 H), 7.95 ("s", 2 H, 2 H, 6 H), 10.09 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.6–31.8 (CH$_2$), 69.3, 73.6 (OCH$_2$), 105.5 (aromat. CH)

123.8, 124.2, 126.5, 130.2 (aromat. CH), 127.1, 127.6, 129.8, 130.7 (olefin. CH), 132.3, 137.4, 137.5, 138.4, 138.8, 138.8 (aromat. C_q, C_qO), 153.4 (C_qO), 192.0 (CHO); FD MS: m/z (%): 1921 (100, $[M+H]^+$), 961 (32, $[M+H]^{2+}$); elemental analysis: calcd for $C_{127}H_{186}O_{13}$: C 79.41, H 9.76; found C 79.43, H 9.86.

(E,E,E,E,E,E)-3,5-Bis{2-{3,5-bis[2-(3,4,5-tridodecyloxyphenyl)ethenyl]phenyl}ethenyl} benzaldehyde (10 c): The preparation was performed as described for **10 a**. Yield: 76%; almost colorless waxy solid with a clearing point at 106 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.87$ (m, 36 H; CH$_3$), 1.24 – 1.86 (m, 240 H; CH$_2$), 3.97, 4.03 (2 t, 24 H; OCH$_2$), 6.74 (s, 8 H; aromat. H), 7.01 (d, $^3J = 16.1$ Hz, 4 H; olefin. H), 7.10 (d, $^3J = 16.1$ Hz, 4 H; olefin. H), 7.24 (d, $^3J = 16.3$ Hz, 2 H; olefin. H), 7.29 (d, $^3J = 16.3$ Hz, 2 H; olefin. H), 7.55 ("s", 6 H; aromat. H), 7.88 ("s", 1 H, 4 H), 7.94 ("s", 2 H, 2 H, 6 H), 10.09 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 14.1$ (CH$_3$), 22.0 – 32.0 (CH$_2$), 69.4, 73.6 (OCH$_2$), 105.6 (aromat. CH), 123.8, 124.3, 126.5, 130.2 (aromat CH), 127.2, 127.7, 129.8, 130.8 (olefin. CH), 132.3, 137.4, 137.5, 138.4, 138.9, 138.9 (aromat. C_q, C_qO), 153.4 (C_qO), 192.0 (CHO); MS (MALDI TOF, Dithranol matrix): m/z (%): 2933 (100, $[M+2H]^+$); elemental analysis: calcd for $C_{199}H_{330}O_{13}$: C 81.55, H 11.35; found C 81.42, H 11.30.

all-(E)-3,5-Bis{2-{3,5-bis{2-{3,5-bis[2-(3,4,5-trihexyloxyphenyl)ethenyl]phenyl}ethenyl}phenyl}ethenyl}benzaldehyde (11 b): The preparation was performed according to the procedure described for **10 a**. The reaction time at room temperature was 7 d. The crude product was first purified by column chromatography (silica gel, petrol ether (40 – 70 °C)/ethyl acetate 7:1) and then by MPLC (silica gel, petrol ether (40 – 70 °C)/ethyl acetate 10:1). Yield 47%; light yellow, glassy solid with a clearing point of 138 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.90$ (m, 72 H; CH$_3$), 1.32, 1.47 (2 m, 144 H; CH$_2$), 1.77 (m, 48 H; CH$_2$), 3.96 (m, 48 H; OCH$_2$), 6.67 (s, 16 H; aromat. H), 6.92 (d, $^3J = 16.1$ Hz, 8 H; olefin. H), 7.02 (d, $^3J = 16.1$ Hz, 8 H; olefin. H), 7.19 (AB, 8 H; olefin. H), 7.22 (AB, 4 H; olefin. H), 7.48, 7.50, 7.55, 7.58 (4 "s", 18 H; aromat. H), 7.85 ("s", 2 H, 2 H, 6 H), 7.92 ("s", 1 H, 4 H), 10.02 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.6 – 31.8 (CH$_2$), 69.2, 73.5 (OCH$_2$), 105.4, 123.7, 124.0, 124.0, 124.9, 126.6, 129.8 (aromat. CH), 127.1, 127.6, 128.5, 129.4, 129.5, 130.4 (olefin. CH), 132.3, 137.4, 137.4, 137.7, 138.2, 138.2, 138.6, 138.6, 153.3 (aromat. C_q, C_qO), 191.9 (CHO); MS (MALDI-TOF, dithranol matrix, CF$_3$CO$_2$Ag): m/z (%): 4047 (100, $[M+Ag]^+$; elemental analysis: calcd for $C_{263}H_{378}O_{25}$: C 80.18, H 9.67; found C 80.16, H 9.59.

all-(E)-3,5-Bis{2-{3,5-bis{2-{3,5-bis{2-{3,5-bis[2-(3,4,5-trihexyloxyphenyl)-ethenyl]phenyl}ethenyl}phenyl}ethenyl}phenyl}ethenyl}benzaldehyde (12 b): The preparation was performed according to the procedure described for **10 a**. The reaction time at room temperature was 10 d. The crude product was purified by column chromatography (basic Al$_2$O$_3$, diethyl ether). Yield: 38%: light yellow, highly viscous oil; ^{1}H NMR (CDCl$_3$): $\delta = 0.87$ (m, 144 H; CH$_3$), 1.24, 1.30, 1.45 (3 m, 288 H; CH$_2$), 1.74 (m, 96 H; CH$_2$), 3.95 (m, 96 H; OCH$_2$), 6.68 (s, 32 H; aromat. H), 6.95 (d, $^3J = 16.4$ Hz, 16 H; olefin. H), 7.05 (d, $^3J = 16.4$ Hz, 16 H; olefin. H), 7.17 – 7.29 (3 AB, 28 H; olefin. H), 7.40 – 7.65 (m, 42 H; aromat. H), 7.78 ("s", 2 H, 2 H, 6 H), 8.01 ("s", 1 H, 4 H), 10.14 (s, 1 H; CHO); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.6 – 31.8 (CH$_2$), 69.2, 73.5 (OCH$_2$), 105.3, 123.7 – 124.9 (aromat. CH), 127.0 – 129.5 (C2, C4, C6, olefin. CH), 132.3, 137.7 – 138.7, 153.3 (aromat. C_q, C_qO, partly superimposed), 191.6 (CHO); MS (MALDI-TOF, dithranol, CF$_3$CO$_2$Ag): m/z (%): 7973 (100, $[M^{+\cdot}]$); elemental analysis: calcd for $C_{535}H_{762}O_{49}$: C 80.55, H 9.63; found C 81.24, H 9.71 (inclusion of solvent).

(E,E,E)-1,3,5-Tris[2-(3,4,5-tripropoxyphenyl)ethenyl]benzene (1^{1}a): Compounds **3** (0.63 g, 1.19 mmol) and **8a** (1.0 g, 3.57 mmol) dissolved in dry THF (10 mL) were slowly added to KOC(CH$_3$)$_3$ (1.0 g, 8.9 mmol) in dry THF (30 mL). The reaction was started under argon at 0 °C, warmed to room temperature and stirred for 12 h. The mixture was then filtered over basic alumina (8 × 5 cm, diethyl ether), the solvent evaporated and the product recrystallized from CH$_2$Cl$_2$, to which ethanol was added, until the solution became turbid. Yield 56%; colorless needles; m.p. 189 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.03$, 1.06 (2 t, 27 H; CH$_3$), 1.83 (m, 18 H; CH$_2$), 3.95, 3.99 (2 t, 18 H; OCH$_2$), 6.74 (s, 6 H; aromat. H), 6.98 (d, $^3J = 16.1$ Hz, 3 H; inner olefin. H), 7.09 (d, $^3J = 16.1$ Hz, 3 H; outer olefin. H), 7.50 (s, 3 H, 2 H, 4 H, 6 H); ^{13}C NMR (CDCl$_3$): $\delta = 10.6$ (CH$_3$), 22.8, 23.5 (CH$_2$), 70.7, 75.1 (OCH$_2$), 105.3 (aromat. CH), 123.5 (C2), 127.3, 129.3 (olefin. CH), 132.4, 138.0, 138.5 (aromat. C_q, C_qO), 153.3 (C_qO); FD MS: m/z (%): 907 (100, $[M+H]^+$); elemental analysis: calcd for $C_{57}H_{78}O_9$: C 75.46, H 8.67; found C 75.56, H 8.60.

(E,E,E)-1,3,5-Tris[2-(3,4,5-trihexyloxyphenyl)ethenyl]benzene (1^{1}b): Prepared analogously to **1^{1}a**. Yield: 55%; colorless, waxy solid with a clearing point at 74 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.91$ (m, 27 H; CH$_3$), 1.20 – 1.60 (m, 54 H; CH$_2$), 1.81 (m, 18 H; CH$_2$), 3.98, 4.02 (2 t, 18 H; OCH$_2$), 6.74 (s, 6 H; aromat. H), 6.98 (d, $^3J = 16.2$ Hz, 3 H; inner olefin. H), 7.10 (d, $^3J = 16.2$ Hz, 3 H; outer olefin. H), 7.51 (s, 3 H, 2 H, 4 H, 6 H); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.0 – 32.0 (CH$_2$), 69.2, 73.5 (OCH$_2$), 105.2 (aromat. CH), 123.5 (C2), 127.3, 129.4 (olefin. CH), 132.4, 138.0, 138.4 (aromat. C_q, C_qO), 153.3 (C_qO); FD MS: m/z (%): 1286 (100, $[M+H]^+$); elemental analysis: calcd for $C_{84}H_{132}O_9$: C 78.46, H 10.35; found C 78.61, H 10.34.

(E,E,E)-1,3,5-Tris[2-(3,4,5-tridodecyloxyphenyl)ethenyl]benzene (1^{1}c): Prepared analogously to **1^{1}a**. Yield 88%; colorless, waxy solid with a clearing point at 75 °C. The analytical data of the compound corresponded to those of an authentic sample.[25]

all-(E)-1,3,5-Tris{2-{3,5-bis[2-(3,4,5-tripropoxyphenyl)ethenyl]phenyl}ethenyl}benzene (1^{2}a): Prepared analogously to **1^{1}a**. Yield 42%; almost colorless crystals; m.p. 161 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.06$ (m, 54 H; CH$_3$), 1.78, 1.85 (2 m, 36 H; CH$_2$), 3.96, 4.00 (2 t, 36 H; OCH$_2$), 6.75 (s, 12 H; aromat. H), 7.02 (d, $^3J = 16.2$ Hz, 6 H; olefin. H), 7.12 (d, $^3J = 16.2$ Hz, 6 H; olefin. H), 7.25 (AB, 6 H; olefin. H), 7.56 ("s", 6 H; aromat. H), 7.63 (s, 3 H, 2 H, 4 H, 6 H); ^{13}C NMR (CDCl$_3$): $\delta = 10.6$ (CH$_3$), 22.8, 23.5 (CH$_2$), 70.9, 75.2 (OCH$_2$), 105.7, 123.8, 123.9, 124.2 (aromat. CH), 127.4, 129.0, 129.3, 129.6 (olefin. CH), 132.4, 138.0, 138.2, 138.3, 138.8 (aromat. C_q, C_qO), 153.4 (C_qO); FD MS: m/z (%): 1022 (78, $[M^{2+}]$), 2042 (100, $[M^{+\cdot}]$); elemental analysis: calcd for $C_{132}H_{168}O_{18}$: C 77.61, H 8.29; found C 77.65, H 8.38.

all-(E)-1,3,5-Tris{2-{3,5-bis[2-(3,4,5-trihexyloxyphenyl)ethenyl]phenyl}ethenyl}benzene (1^{2}b): Prepared analogously to **1^{1}a**. The crude product was purified by column chromatography (silica gel 8 × 20 cm, petrol ether (40 – 70 °C)/ethyl acetate 10:1). Yield 71%; almost colorless, waxy solid with a clearing point at 144 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.89$, 0.90 (2 t, 54 H; CH$_3$), 1.33, 1.48 (2 m, 108 H; CH$_2$), 1.75, 1.82 (2 m, 36 H; CH$_2$), 3.98, 4.03 (2 t, 36 H; OCH$_2$), 6.75 (s, 12 H; aromat. H), 7.03 (d, $^3J = 16.2$ Hz, 6 H; olefin. H), 7.12 (d, $^3J = 16.3$ Hz, 6 H; olefin. H), 7.25 (AB, 6 H; olefin. H), 7.56 ("s", 6 H; aromat. H), 7.57 ("s", 3 H; aromat. H), 7.62 (s, 3 H, 2 H, 4 H, 6 H); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.6 – 31.8 (CH$_2$), 69.4, 73.6 (OCH$_2$), 105.6, 123.8, 123.8, 124.2 (aromat. CH), 127.4, 129.0, 129.4, 129.7 (olefin. CH), 132.4, 138.0, 138.2, 138.3, 138.8 (aromat. C_q, C_qO), 153.4 (C_qO); MS (MALDI-TOF, dithranol, CF$_3$CO$_2$Ag: m/z (%): 2908 (100, $[M+Ag]^+$); elemental analysis: calcd for $C_{186}H_{276}O_{18}$: C 79.78, H 9.93; found C 79.76, H 9.86.

all-(E)-1,3,5-Tris{2-{3,5-bis[2-(3,4,5-tridodecyloxyphenyl)ethenyl]phenyl}ethenyl}benzene (1^{2}c): The preparation was performed according to the procedure described for **1^{1}a**; however, the reaction time amounted to 24 h. The crude product was filtered over basic Al$_2$O$_3$ with diethyl ether as the eluant. Yield 70%, almost colorless, waxy solid with a clearing point of 99 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.85$, (m, 54 H; CH$_3$), 1.23 – 1.85 (m, 360 H; CH$_2$), 3.98, 4.03 (2 t, 36 H; OCH$_2$), 6.75 (s, 12 H; aromat. H), 7.03 (d, $^3J = 16.2$ Hz, 6 H; olefin. H), 7.12 (d, $^3J = 16.3$ Hz, 6 H; olefin. H), 7.25 (AB, 6 H; olefin. H), 7.56 ("s", 6 H; aromat. H), 7.57 ("s", 3 H; aromat. H), 7.62 (s, 3 H, 2 H, 4 H, 6 H); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$ (CH$_3$), 22.3 – 31.8 (CH$_2$), 69.4, 73.6 (OCH$_2$), 105.6, 123.8, 123.9, 124.2, (aromat. CH), 127.3 129.0, 129.4, 129.7 (olefin. CH), 132.4, 138.0, 138.2, 138.3, 138.8 (aromat. C_q, C_qO), 153.4 (C_qO); MS (MALDI-TOF, dithranol: m/z (%): 4315 (100, $[M^{+\cdot}]$); elemental analysis: calcd for $C_{294}H_{492}O_{18}$: C 81.83, H 11.49; found C 82.07, H 11.18.

all-(E)-1,3,5-Tris{2-{3,5-bis{2-{3,5-bis[2-(3,4,5-tripropoxyphenyl)ethenyl]phenyl}ethenyl}phenyl}ethenyl}benzene (1^{3}a): The preparation was performed according to the procedure described for **1^{1}a**; however, NaH was used instead of KOC(CH$_3$)$_3$. After 1 h at ambient temperature the reaction mixture was refluxed for 2 h and then quenched with water and 2 M HCl. The crude product was purified by column chromatography (silica gel 3 × 30 cm, petrol ether (40 – 70 °C)/ethyl acetate 10:1). Yield: 28%; glassy, yellowish solid; m.p. 142 °C; ^{1}H NMR (CDCl$_3$, 313 K): $\delta = 0.95$, 1.02 (2 t, 108 H; CH$_3$), 1.73 (m, 72 H; CH$_2$), 3.94 (m, 72 H; OCH$_2$), 6.70 (s, 24 H; aromat. H), 6.93 (d, $^3J = 16.1$ Hz, 12 H; olefin. H), 7.02 (d, $^3J = 16.1$ Hz, 12 H; olefin. H), 7.25 (AB, 12 H; olefin. H), 7.29 (AB, 6 H; olefin. H), 7.47 (m, 6 H; aromat. H), 7.52 (m, 12 H; aromat. H), 7.58, 7.64, 7.67 (3 m, 12 H; aromat. H); ^{13}C NMR (CDCl$_3$): $\delta = 10.5$ (CH$_3$), 22.8, 23.5 (CH$_2$), 70.7, 75.1 (OCH$_2$), 105.4 (aromat. CH), 123.6 – 124.1 (aromat. CH, partly superimposed), 127.1, 128.4, 128.9, 129.0, 129.2, 129.4 (olefin. CH), 132.3, 137.6 – 138.5 (aromat. C_q, C_qO, partly superimposed), 153.3 (C_qO); MS (MALDI-

TOF, dithranol): m/z (%): 4314 (100, $[M^{+\cdot}]$); elemental analysis: calcd for $C_{282}H_{348}O_{36}$: C 78.52, H 8.13; found C 78.50, H 8.14.

all-(*E*)-1,3,5-Tris{2-{3,5-bis{2-{3,5-bis[2-(3,4,5-trihexyloxyphenyl)ethenyl]-phenyl}ethenyl}phenyl}ethenyl}benzene (1³b): Prepared analogously to **1¹a**; the reaction time was 12 h at room temperature. Column filtration was performed on silica gel (8 × 20 cm) with petrol ether (40–70 °C)/ethyl acetate 15:1. Yield 61 %, glassy, colorless compound (glass transition at −45 °C); ¹H NMR (CDCl₃): $\delta = 0.87$ (m, 108 H; CH₃), 1.20–1.50 (m, 216 H; CH₂), 1.74 (m, 72 H; CH₂), 3.94 (m, 72 H; OCH₂), 6.60–6.80 (m, 24 H; aromat. H), 6.80–7.10 (AB, 24 H; olefin. H), 7.26, 7.30, (2 AB, 18 H; olefin. H), 7.40–7.70 (m, 30 H; aromat. H); ¹³C NMR (CDCl₃): $\delta = 14.0$ (CH₃), 22.6–31.8 (CH₂), 69.3, 73.5 (OCH₂), 105.5, 123.7–124.1, 125.1 (aromat. CH, partly superimposed), 127.2, 128.7–129.4, 129.6 (olefin. CH, partly superimposed), 132.4, 137.9–138.8 (aromat. C_q, C_qO, partly superimposed), 153.4 (C_qO); MS (MALDI-TOF, dithranol, CF₃CO₂Ag): m/z (%): 5936 (100, $[M+Ag]^+$); elemental analysis: calcd for $C_{390}H_{564}O_{36}$: C 80.37, H 9.75; found C 80.42, H 9.79.

all-(*E*)-1,3,5-Tris{2-{3,5-bis{2-{3,5-bis[2-(3,4,5-tridodecyloxyphenyl)ethenyl]-phenyl}ethenyl}phenyl}ethenyl}benzene (1³c): Prepared analogously to **1¹a**; the reaction time was 24 h at room temperature. Basic alumina and diethyl ether were used for the column chromatography. Yield: 17%; almost colorless oil; ¹H NMR (CDCl₃): $\delta = 0.83$ (t, 108 H; CH₃), 1.20–1.90 (m, 720 H; CH₂), 3.80–4.10 (m, 72 H; OCH₂), 6.69 (s, 24 H; aromat. H), 6.97 (d, $^3J = 16.1$ Hz, 12 H; olefin. H), 7.07 (d, $^3J = 16.1$ Hz, 12 H; olefin. H), 7.27 (AB, 12 H; olefin. H), 7.34 (AB, 6 H; olefin. H), 7.53 ("s", 6 H; aromat. H), 7.55 ("s", 12 H; aromat. H), 7.62–7.71 (m, 12 H; aromat. H); ¹³C NMR (CDCl₃): $\delta = 14.1$ (CH₃), 22.0–32.0 (CH₂), 69.3, 73.6 (OCH₂), 105.6, 123.7–124.6 (aromat. CH, partly superimposed), 127.3, 128.8, 129.1, 129.4, 129.4, 129.7 (olefin. CH), 132.4, 137.8–138.8, (aromat. C_q, C_qO, partly superimposed), 153.4 (C_qO); MS (MALDI-TOF, dithranol): m/z (%): 8859 (100, $[M^{+\cdot}]$); elemental analysis: calcd for $C_{606}H_{996}O_{36}$: C 82.17, H 11.33; found C 82.18, H 11.28.

all-(*E*)-1,3,5-Tris{2-{3,5-bis{2-{3,5-bis{2-{3,5-bis[2-(3,4,5-trihexyloxyphenyl)-ethenyl]phenyl}ethenyl}phenyl}ethenyl}phenyl}ethenyl}benzene (1⁴b): Prepared analogously to **1¹a**; the reaction time was 10 d. The same work-up as for **1³c** was used. Yield: 38 %, light yellow oil; ¹H NMR (CDCl₃): $\delta = 0.86$ (m, 108 H; CH₃), 1.20–1.78 (m, 576 H; CH₂), 3.93 (m, 144 H; OCH₂), 6.63–6.74 (m, 48 H; aromat. H), 6.88–7.29 (4 AB, 90 H; olefin. H), 7.46–7.58 (m, 66 H; aromat. H); ¹³C NMR (CDCl₃): $\delta = 14.0$ (CH₃), 22.6–31.8 (CH₂, partly superimposed), 69.2, 73.5 (OCH₂), 105.4, 123.5–124.5 (aromat. CH, partly superimposed), 127.2–129.4 (olefin. CH, partly superimposed), 132.3, 137.8–138.6 (aromat. C_q, C_qO, partly superimposed), 153.3 (C_qO); MS (MALDI-TOF, dithranol, CF₃CO₂Ag): m/z (%): 11993 (100, $[M+Ag]^+$); elemental analysis: calcd for $C_{798}H_{1140}O_{72}$: C 80.64, H 9.67; found C 80.67, H 9.74.

all-(*E*)-1,3,5-Tris{2-{3,5-bis{2-{3,5-bis{2-{3,5-bis{2-(3,4,5-trihexyl-oxyphenyl)ethenyl]phenyl}ethenyl}phenyl}ethenyl}phenyl}ethenyl}phenyl}-ethenyl}benzene (1⁵b): Prepared analogously to **1¹a**; however, NaH was used instead of KOC(CH₃)₃. The reaction time was 18 d. The crude product was purified by column chromatography (silica gel, toluene/ethyl acetate 9:1). Raw yield: 77%, light yellow oil; ¹H NMR (CDCl₃): $\delta = 0.89$ (m, 432 H; CH₃), 1.27–1.84 (m, 1152 H; CH₂), 3.90–4.05 (m, 288 H; OCH₂), 6.64–7.63 (m, 420 H; aromat. and olefin. H); ¹³C NMR (CDCl₃): $\delta = 14.2$ (CH₃), 19.9–37.8 (CH₂, partly superimposed), 69.5, 73.8 (OCH₂), 105.6, 124.1–125.9 (aromat. CH, partly superimposed), 127.5–129.9 (olefin. CH, partly superimposed), 132.7, 138.4–139.0 (aromat. C_q, C_qO, partly superimposed), 153.7 (C_qO); MS (MALDI-TOF, dithranol, CF₃CO₂Ag): m/z (%): 24290 (100, $[M+Ag+2C_7H_8]^+$); [16] elemental analysis: calcd for $C_{1614}H_{2292}O_{144}$: C 80.77, H 9.63; found C 82.08, H 9.39.[15]

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[15] The yields in Scheme 3 correspond to the purified compounds except for **1⁵b** where the raw product resisted a complete purification. Toluene, in particular, was so strongly captured in the cavities of the dendrimer that it could not be totally removed in the vacuum. See also [16].

[16] The desorbed ion contains two molecules toluene.

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