

## Dendrimers Consisting of Stilbene or Distyrylbenzene Building Blocks Synthesis and Stability

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**Abstract:** On the basis of Wittig-Horner reactions and protection group techniques compound **7** for the core and the components **9a-c** and **11a-c** for the dendrons were prepared and linked in the final step. The convergent synthesis yielded constitutionally and configurationally pure dendrimers (**2a-c**, **2a'-c'**) which consist of distyrylbenzene units. Their thermo-oxidative stability in the presence of air was studied by chemiluminescence and compared to the dendrimers **1** consisting of stilbene units. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Dendrimers; Wittig reactions; oxidation; chemiluminescence

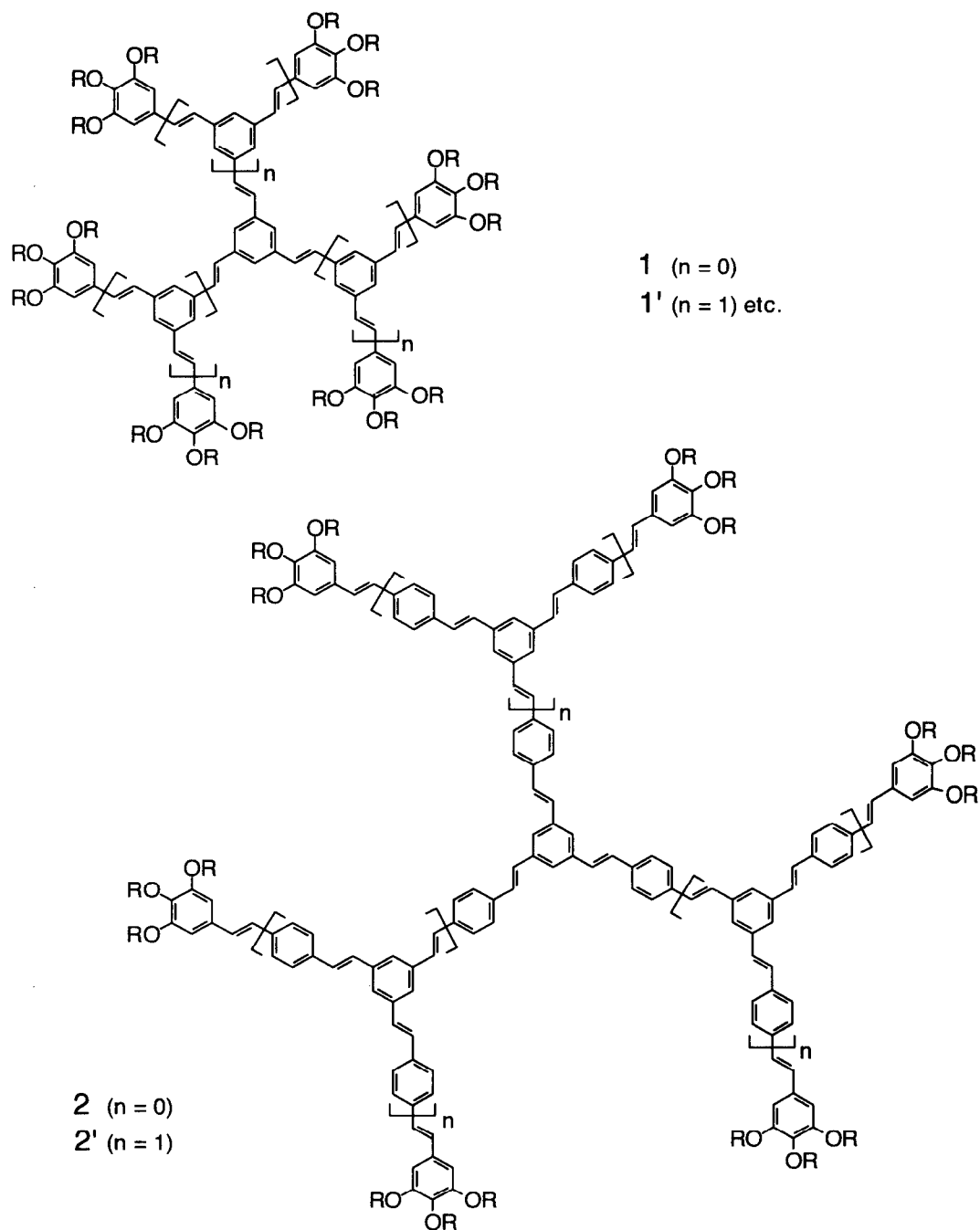
### Introduction

Dendrimers play an important role with a steadily increasing interest in synthetic chemistry and materials science.<sup>1</sup> Recently we reported on a strategy to synthesize the dendrimers **1** with a scaffold of stilbene building blocks.<sup>2</sup> Until now we prepared with a convergent, between the generations coupled synthesis five generations.<sup>3</sup> The first two generations exhibit columnar liquid crystalline phases.<sup>2</sup> Since stilbenes have a rather large HOMO-LUMO gap (band gap), which seems to be unfavorable for applications as photoconductors or in light emitting diodes,<sup>4</sup> we wanted to decrease the band gap by extension of the conjugation of the building blocks. For this purpose we prepared the dendrimers **2** with distyrylbenzene units. Moreover, we investigated their thermal properties and their resistance against oxygen in comparison to the dendrimers **1**. Extremely sensitive methods are required to study the stability of compounds aimed for photo- and electro-optical applications since minor structural changes can lead to a considerable loss of functionality. Chemiluminescence (CL) provides a powerful tool to determine selectively the oxidative degradation of organic compounds.<sup>5,6,7,8,9</sup> Hereby the CL intensity is proportional to the reaction rate and the single photon counting technique permits an extremely sensitive monitoring of the thermo-oxidative behavior at temperature ranges and degrees of degradation much below those accessible by alternative methods such as FT IR and thermogravimetry (TG).

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Hence, CL is a promising method in the area of functional, conjugated organic compounds.<sup>10,11,12</sup> The corresponding loss of the relevant functional properties can be checked by UV/Vis spectroscopy.

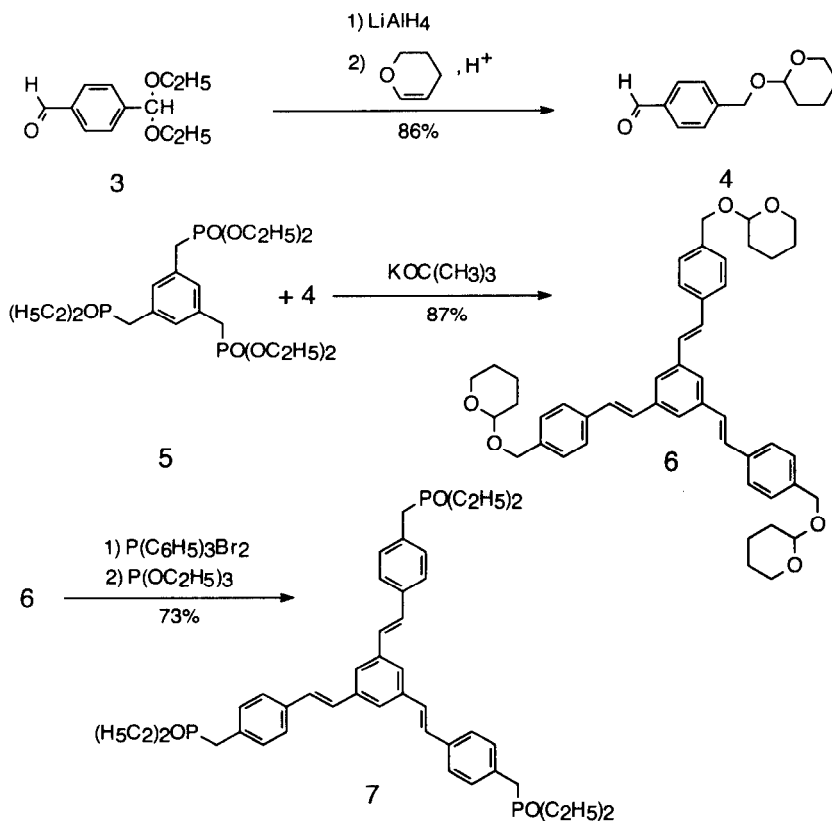
**Scheme 1**



## Results and Discussion

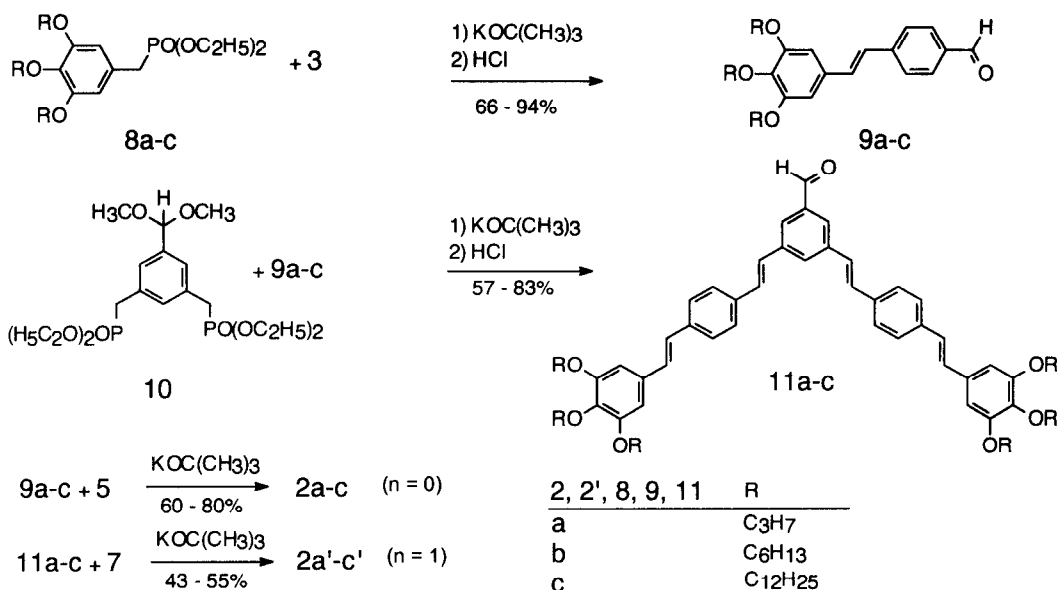
The convergent synthesis of the dendrimers **2** consisted of separate preparations of the core and the dendrons and the attachment of the dendrons to the core in the final reaction step. The monoprotected terephthalaldehyde **3** was reduced to the corresponding alcohol and the hydroxy group protected as tetrahydropyran-2-yl ether **4**.<sup>13</sup> The Wittig-Horner reaction of the triphosphonate **5**<sup>2</sup> yielded with **4** the tristyrylbenzene derivative **6** which could be transformed to the extended triphosphonate **7**. Triphenylphosphine dibromide served thereby for the intermediate formation of bromomethyl groups which reacted then with triethyl phosphite.

Scheme 2



The preparation of the dendrons was performed by Wittig-Horner reactions of the monophosphonate **8**<sup>3</sup> and the diphosphonate **10**<sup>2,3</sup> with the aldehydes **3** and **9a-c**, respectively. The (*E*) selectivity of the formation of the CC double bonds proved to be sufficiently high, so that (*Z*) configurations could not be detected in the <sup>1</sup>H NMR spectra of the purified compounds **9a-c** and **11a-c**. The dendrimers **2a-c** and **2a'-c'** could be obtained in the final olefination steps **9a-c** → **2a-c** and **11a-c** → **2a'-c'**. The yields range between 60 and 80% for the compounds **2a-c** of the first generation and drop to 43 – 55% for the second generation (**2a'-c'**).

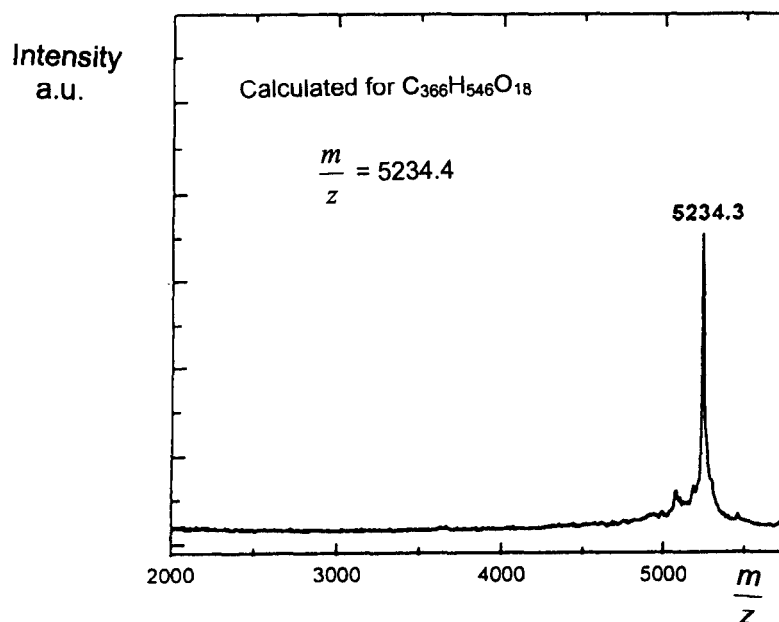
## Scheme 3



Due to the convergent synthesis the dendrimers **2a-c** and **2a'-c'** could be obtained in a constitutionally and configurationally pure state; they were comprehensively characterized by spectroscopic means. The <sup>1</sup>H NMR spectra showed a typical behavior for the olefinic protons. Their  $\delta$  values in CDCl<sub>3</sub> increase from 6.95 to 7.27 on going from the outer double bonds to the centre; simultaneously the AB pattern degenerates more and more in the direction of an A<sub>2</sub> singlet. The vicinal coupling constants of  $16.1 \pm 0.3$  Hz prove the (*E*) configurations. The aromatic protons on the peripheral, alkoxy-substituted rings give rise to singlet signals at 6.66 – 6.76 ppm. The other aromatic protons represent AA'BB', A<sub>2</sub>B, or A<sub>3</sub> singlet spin systems with resonances between 7.25 and 7.63 ppm. The compounds **2a'-c'** of the second generation give broad signals because of the aggregation and the reduced mobility of the whole molecules and the molecule segments. In order to get a resolved spectrum, we additionally measured **2c'** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 140 °C. The outer olefinic protons (12 H) showed an AB spin pattern at 6.98/ 7.04 (<sup>3</sup>*J* = 16.2 Hz), whereas the other olefinic protons gave superimposed AB spin patterns between 7.19 and 7.26 ppm ( $15.9 \text{ Hz} \leq {}^3J \leq 16.2 \text{ Hz}$ ). In the aromatic region 24 H gave rise to an AA'BB' spin system centered at 7.54 ppm, representing six *p*-substituted benzene rings, and the other inner 24 aromatic protons led to a multiplet between 7.58 and 7.63 ppm. The singlet for the protons at the peripheral rings was obtained at  $\delta = 6.76$ . A detailed correlation of the <sup>1</sup>H and <sup>13</sup>C NMR data is given in the Experimental Section.

The MALDI-TOF technique provided an excellent tool for the determination of the molecular masses of **2b'** and **2c'** whereas the FD method worked for the lower systems. Figure 1 shows as an example the MALDI-TOF spectrum of **2c'**. It demonstrates the absence of dendrimers which contain only one or two dendrons; thus, it can be used for the control of the last reaction step.

The molecular structures contain large cavities (Scheme 1); so they do not represent typical discotic mesogens. Nevertheless, almost all compounds **2** and **2'** show a liquid crystalline phase above room temperature. The only exception is **2a** which reveals a transition of the crystalline state (Cr) to the isotropic melt (I) at 216 °C. The results of the differential scanning calorimetry (DSC) are summarized in Table 1.



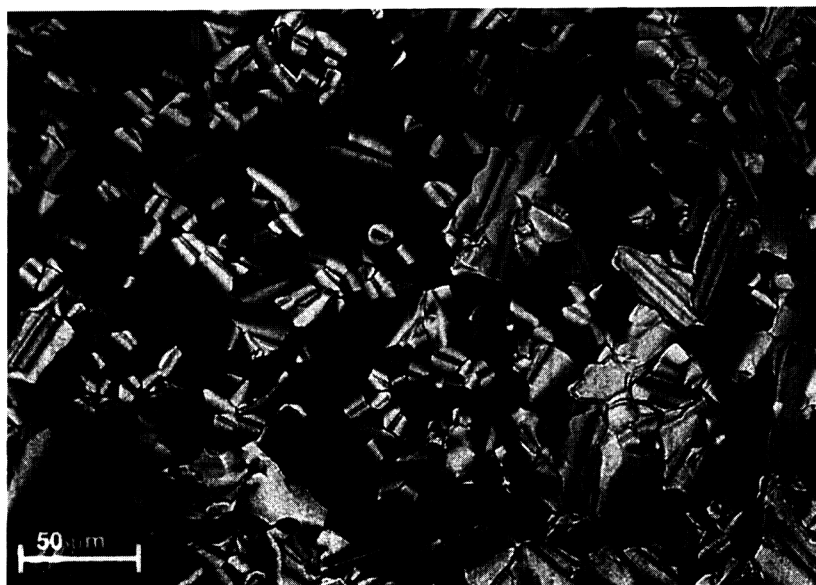
**Figure 1.** MALDI-TOF spectrum of compound **2a'**. Measurement in a 1,8,9-trihydroxyanthracene (dithranol) matrix with a pulsed N<sub>2</sub> laser ( $\lambda = 337$  nm).

**Table 1.** Phase transitions of the dendrimers **2a-c** and **2a'-c'** measured by differential scanning calorimetry. (Onset temperatures of the second heating curve  $T$  [°C],  $\Delta H$  [kJ · mol<sup>-1</sup>], Cr: crystalline phase, G: glassy phase, M: mesophase, Col: columnar phase, Col<sub>hd</sub>: disordered hexagonal columnar phase, Col<sub>ob</sub>: oblique columnar phase, L<sub>D</sub>: lamellar phase, I: isotropic phase)

Dendrimer	Cr	G	T	$\Delta H$	G	T	$\Delta H$	M	T	$\Delta H$	I
<b>2a</b>	◆		216	40							◆
<b>2b</b>		◆	-42(T <sub>g</sub> )		◆	24	(T <sub>g</sub> )	L <sub>D</sub>	129	3	◆
<b>2c</b>	◆		-35	31	◆	21	(T <sub>g</sub> )	Col <sub>hd</sub>	108	4	◆
<b>2a'</b>		◆	102(T <sub>g</sub> )					Col	254 <sup>a)</sup>	1	◆
<b>2b'</b>		◆	-61(T <sub>g</sub> )					Col <sub>hd</sub>	235	5	◆
<b>2c'</b>	◆		-27	63				Col <sub>ob</sub>	195	6	◆

<sup>a)</sup>First heating curve, since the compound starts to decompose at the clearing point

The dendrimers **2b,c,a'-c'** show between crossed polarizers mosaic textures, which are typical for columnar phases. Figure 2 presents the texture of **2c** as an example. Additionally X-ray diffraction experiments<sup>14</sup> were used to ascertain the structures of the mesophases Col<sub>hd</sub>, Col<sub>ob</sub> and L<sub>D</sub>.



**Figure 2.** Mosaic texture of compound **2c**, measured at 95 °C in the Col<sub>hd</sub> phase.

All dendrimers **2** and **2'** exhibit in dichloromethane UV absorptions with maxima at 375 nm. In comparison to the dendrimers **1**, the maxima are bathochromically shifted by 45 nm. This effect corresponds to a decreased HOMO-LUMO gap caused by the extended conjugation. Using an excitation wavelength of 337 nm (N<sub>2</sub> laser), a photocurrent was observed in the LC phase of **2c'**; the corresponding dendrimer **1c'** (n = 1, R = C<sub>12</sub>H<sub>25</sub>) did not show photoconductivity.<sup>14</sup> The larger HOMO-LUMO gap in the series **1**<sup>(s)</sup> (band gap in the solid state) leads to a higher barrier for the generation of charge carriers.

An important point of interest is the stability of the dendrimers. Thermogravimetry measurements of **1c'** and **2c'** revealed that these compounds decompose at temperatures above 300 °C. (Figure 3)

In the low temperature region between room temperature and 180 °C, which is of interest for many applications of materials, we examined **1c'** and **2c'** in the presence of air by a more sensitive method which makes use of the chemiluminescence (CL). The behavior of **1c'** and **2c'** is closely related to the characteristics found in CL experiments with poly(1,4-phenylenevinylene)s (PPV).<sup>10,11,15</sup> It can be rationalized as a superposition of four different processes. The used temperature profiles and the resulting CL intensities are depicted in the figures 4, 5 and 7.

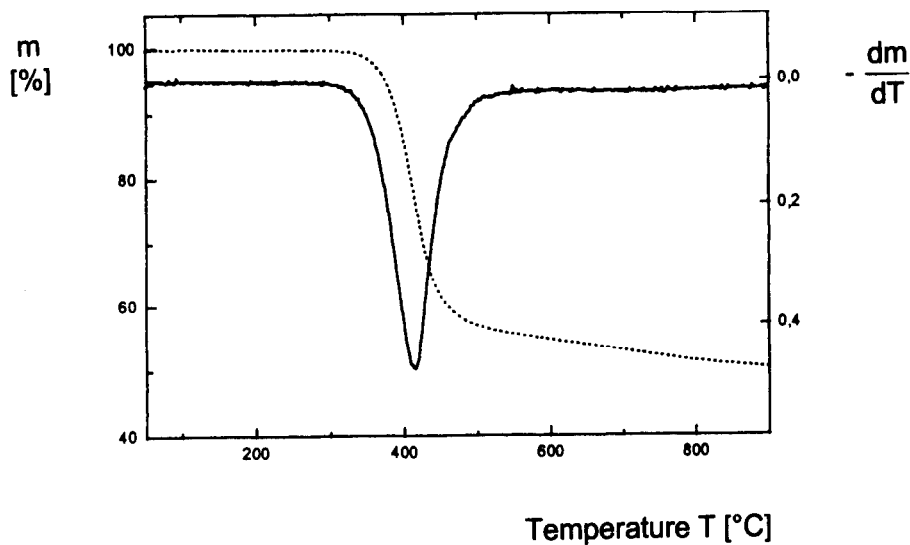


Figure 3. Thermogravimetry of compound **1c'**. Heating curve with loss of mass  $m$  (.....), first derivative (—).

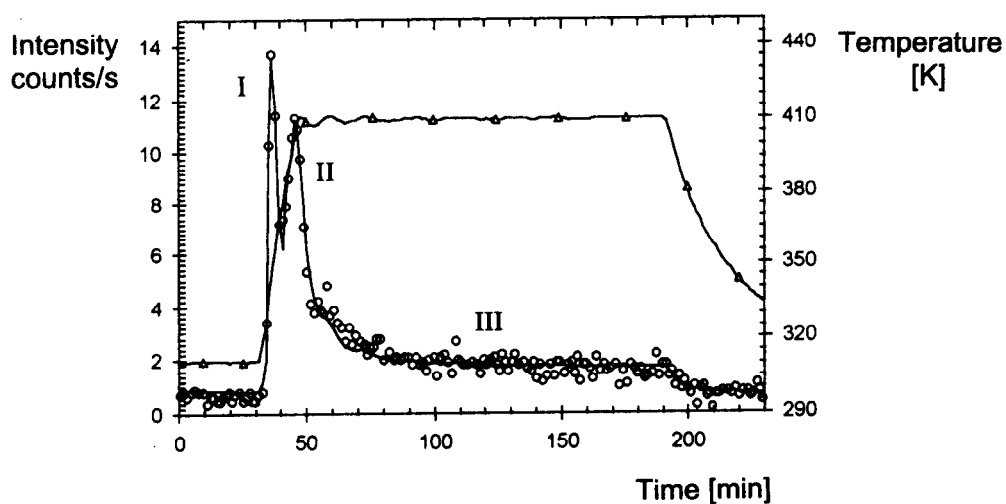
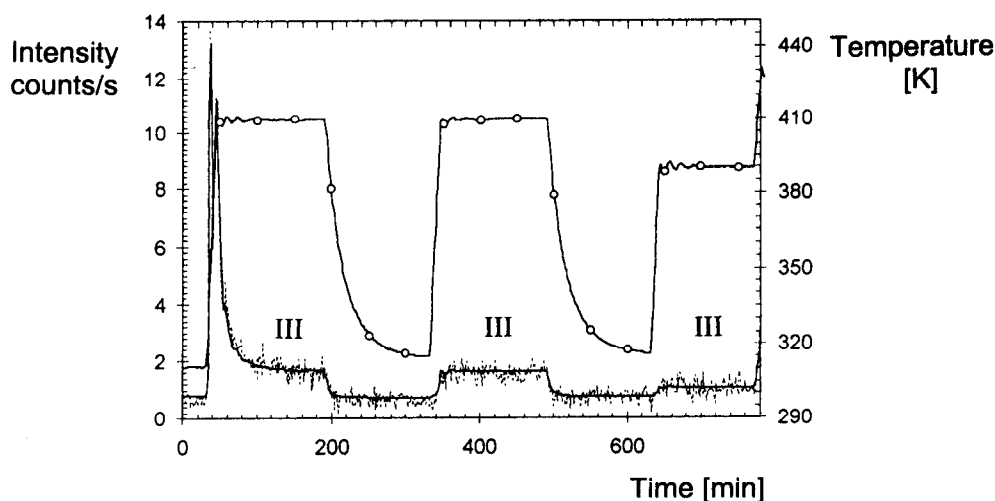


Figure 4. Time-dependent temperature profile ( $-\Delta-$ ) and CL intensity ( $-o-$ ) for the first heating period of compound **1c'** showing peak I, peak II and the subsequent plateau III.

The first heating period revealed three processes (peak I, peak II and plateau III in Figure 4); I and II indicated the consumption of one or more reacting components. Consequently these two peaks were not ob-



**Figure 5.** Temperature profile (-o-) and CL intensity versus time for the first three heating periods of compound **1c'**.

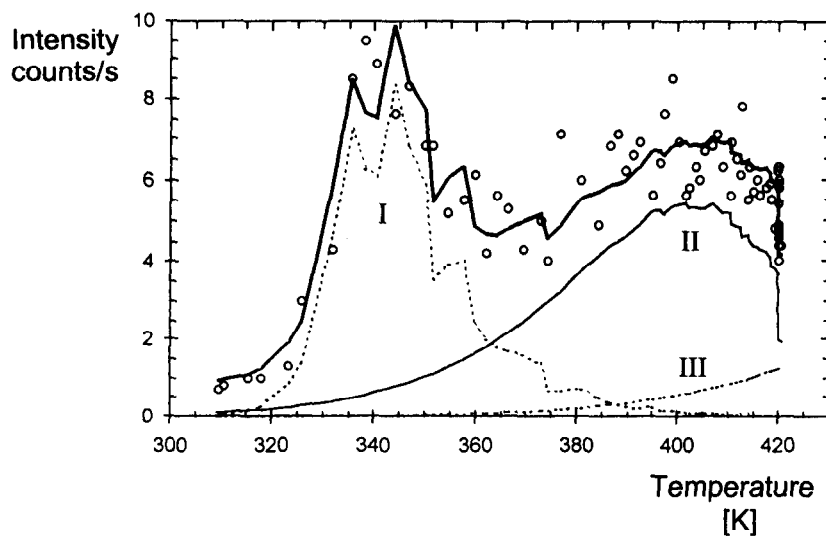
served in the consecutive heating cycles (Figure 5). In the PPV series this behavior was assigned to the reactions with oxygen dissolved in the probe<sup>10,11</sup>. The process corresponding to peak I is a bulk feature since the intensity is proportional to the thickness  $d$  of the films which was varied between 1 and 40  $\mu\text{m}$ . Furthermore, the peak is sharp in the time scale as well as in the temperature scale and was not changed or shifted by decreasing the heating rate. It was not possible to fit peak I based on reaction kinetics of first or second order. For higher orders the fit became satisfactory and activation energies of  $175 \pm 25 \text{ kJ} \cdot \text{mol}^{-1}$  were determined.

The integral CL intensity of peak II increased also with increasing thickness of the films; however, a proportionality could not be established. It is reasonable to identify peak II as a bulk feature, too. Lower heating rates resulted in a clear broadening of the peak. It could be accurately fitted by a thermally activated reaction with second order kinetics in one reactant. The activation energy was determined to be  $61 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ .

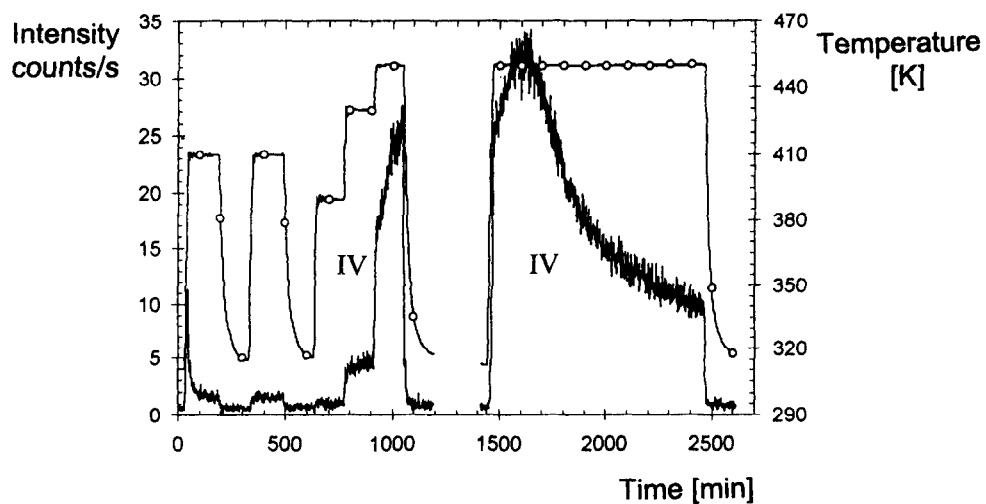
All samples showed a plateau III (Figures 4, 5). The CL intensity in this period was nearly constant versus time and did not depend on the thickness of the samples. The activation energies were calculated to be  $68 \pm 10 \text{ kJ} \cdot \text{mol}^{-1}$  based on first order kinetics. As a possible process we propose a transport-limited reaction with oxygen diffusing into the sample with a constant rate. Figure 6 shows a fit of the three processes I, II and III and their superposition.

The description of the thermooxidation behavior of **1c'**, based on a superposition of the three processes mentioned above, is satisfactory until a further process IV (Figure 7) occurs. Process IV was characterized by





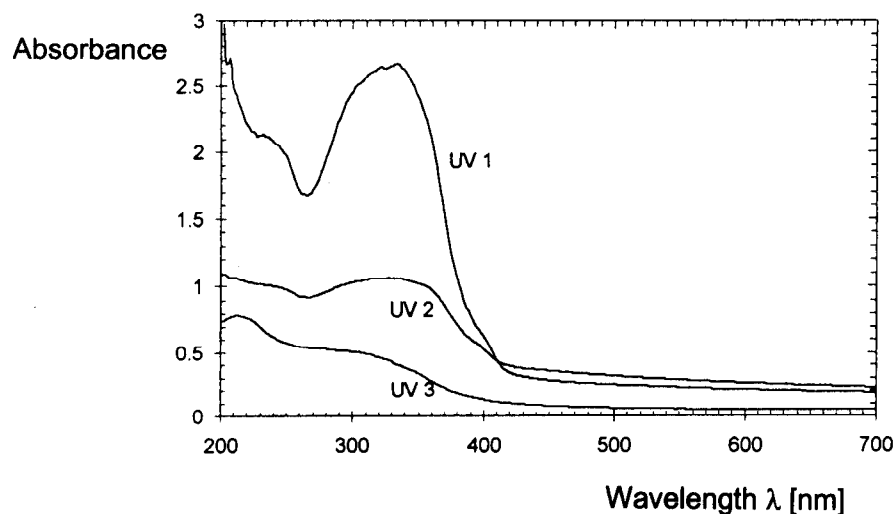
**Figure 6.** CL intensities and data fits for the processes I, II and III versus temperature for the first heating period of compound 1c'. The thick line represents the superposition of the three individual fits.



**Figure 7.** Temperature profiles (-o-) and CL intensities which characterize the autoxidation process IV of compound 1c'.

an induction period and a peak behavior which is typical for autoxidation reactions. With increasing tempera-

ture the induction time decreased. Similar CL characteristics are well known, e.g. for thermooxidative degradation of polyethylene.<sup>9</sup> This process is not general for all PPV derivatives, but was determined for 2-ethylhexyloxy-substituted PPV.<sup>15</sup> We assume that the origin of the fourth process is an oxidation of the OC<sub>12</sub>H<sub>25</sub> chains. The corresponding intensities are found to be similar to the intensities of the other processes, indicating a high efficiency for the molecular CL process. This is not surprising, because stilbenoid chromophores can act as acceptors for the excitation energy; thus the CL quantum yield can be increased.



**Figure 8.** UV/Vis spectra before the CL experiment (UV 1), after the first heating period (UV 2) and at the end (2600 min) of the CL experiment (UV 3). Measurement of the neat films.

The CL measurements of **2c'** gave analogous results; therefore further figures can be omitted. Moreover, both compounds showed similar characteristics as the previously investigated PPV derivatives. Nevertheless, some small differences between **1c'** and **2c'** shall be mentioned. The fourth process occurred at lower temperatures for **2c'** in comparison to **1c'**. Furthermore, the CL intensities of **2c'** were considerable higher than those of **1c'**. We conclude that **1c'** forms more stable films compared to **2c'**. It is reasonable that the compound with the smaller band gap has the higher sensitivity towards oxygen.

The reported oxidation processes, especially the fourth process involving the OC<sub>12</sub>H<sub>25</sub> substituents, are not necessarily associated with a loss of functional properties. As a tentative function, UV/VIS absorption was chosen revealing small changes of chromophores which are important for properties like fluorescence, electroluminescence or photoconductivity. Due to light scattering, the UV/VIS spectra (Figure 8) of the films showed a large background at  $\lambda > 420$  nm, in particular for the spectra measured before the CL experiments. Afterwards this contribution is reduced because the surfaces were smoothed at high temperatures. Figure 8

illustrates a typical series of UV/Vis spectra measured during the investigations of **1c'**. It is important to note that already the first heating cycle resulted in a drastic decrease of the absorbance of the samples. Obviously, a major part of the olefinic double bonds had already reacted. The UV/Vis measurements provide strong evidence for the relevance of the early stages of thermo-oxidative degradation monitored by means of the CL technique. It is apparent that oxidation processes leading to a drastic loss of the functional properties of stilbenoid derivatives were detected at temperatures far below the temperatures at which a degradation process was measured by TG experiments.

### Conclusions

The synthetic strategy for the preparation of the stilbenoid dendrimer **1**<sup>(s)</sup> proved also to be suitable for the generation of the dendrimers **2**<sup>(s)</sup> consisting of *p*-distyrylbenzene building blocks. Long, flexible alkoxy chains induce in both series the thermotropic generation of LC phases.

The UV/Vis absorption maxima of the dendrimers **2**<sup>(s)</sup> with the extended conjugation length are bathochromically shifted in comparison to the maxima of the dendrimers **1**<sup>(s)</sup>. Thus the band gap energy is decreased which is important for an application in photoconducting devices. However, this property influences also the thermo-oxidative stability of the materials which was investigated by chemiluminescence (CL). Degradation occurred at temperatures far below those manifested by thermogravimetry measurements (TG). The relevance of the early stages of degradation to the functional properties was shown by UV/Vis spectroscopy. We found four distinct processes with clearly different characteristics. Three of them seem to be directly connected with the consumption of a major part of the double bonds in thin films of **1c'** and **2c'**. We have to conclude that a direct contact to oxygen has to be avoided during operation as well as during processing in respect to the long term stability required for a reasonable application of stilbenoid dendrimers.<sup>16</sup>

### Experimental Section

#### General methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by using Bruker AC 200, AM 400 and DRX-500 spectrometers. Mass spectra were obtained on Varian MAT CH7A (EI), Finnigan MAT 95 (FD) or Bruker Reflex (MALDI-TOF) spectrometers. IR spectra were recorded on a Beckman Acculab 4 spectrometer. UV/VIS spectra were measured with a Zeiss MCS 320/340 diode array spectrograph. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC 7. Thermogravimetric measurements were done with a Mettler TG 50. Melting points are uncorrected if not measured by DSC.

### CL Experiments

The CL experimental set-up consisted of a sample holder, a photomultiplier and the single photon counting electronic equipment and was described in detail elsewhere.<sup>11</sup> All CL experiments were performed under air. The samples were heated consecutively to distinct plateau temperatures (390 K, 410 K, 430 K or 450 K). The temperatures were maintained for periods of more than 100 min before the probes were cooled down to room temperature or heated to the next plateau temperature. The alternation of isothermal and heating-up experiments as well as the variation of the heating rates was chosen to obtain a meaningful insight in the time-temperature-dependence of the thermo-oxidative behavior. The complete experiments took about 2 d for each sample. The absorption spectra of the samples were recorded with a UV/Vis spectrometer (Zeiss DMR10) before and after the CL experiments. In order to compare the two dendrimer series, **1c'** (n = 1, R = C<sub>12</sub>H<sub>25</sub>) and **2c'** (n = 1, R = C<sub>12</sub>H<sub>25</sub>) were investigated by CL. For each material four samples were prepared from solution, whereby the thickness of the solid films was varied by dropping different amounts of the dissolved probes on quartz substrates followed by evaporation of the solvent.

### Preparations

**(±)-4-(3,4,5,6-Tetrahydro-2H-pyran-2-yloxymethyl)benzaldehyde (4)**: 40.0 g (192 mmol) of terephthalaldehyde monodiethylacetal **3** was added slowly to a suspension of 3.0 g (79 mmol) of LiAlH<sub>4</sub> in 200 ml of dry diethyl ether. The mixture was refluxed for 2 h and then cooled with an ice bath before 400 ml of water was slowly added. The two layers were separated and the aqueous phase was extracted twice with 100 ml of diethyl ether. The collected organic extracts were treated with 200 ml of 2 M HCl for about 5 min. The organic layer was separated, washed with 100 ml of water and dried over MgSO<sub>4</sub> before the solvent was evaporated. To the residue consisting of 20.4 g (78 %) oily 4-hydroxymethylbenzaldehyde, 23.0 g (270 mmol) of dihydropyran, 8.77 g (35 mmol) of pyridinium p-toluenesulfonate (PPTS) and 300 ml of dry CH<sub>2</sub>Cl<sub>2</sub> were added. The mixture was stirred for 48 h at room temperature, washed with 100 ml of brine and dried over MgSO<sub>4</sub>. The solvent was removed to give 32.9 g (78 % related to **3**) of **4**, a colorless liquid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 1.50 - 1.90 (m, 6 H, CH<sub>2</sub>), 3.54/ 3.87 (m, 2 H, OCH<sub>2</sub> (THP)), 4.56/ 4.85 (AB, 2 H, ArCH<sub>2</sub>O), 4.71 (t, 1 H, OCH), 7.51/ 7.84 (AA'BB', 4 H), 9.98 (s, 1 H, CHO). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 19.3/ 25.4/ 30.5 (CH<sub>2</sub>), 62.2/ 68.1 (OCH<sub>2</sub>), 98.2 (OCH), 127.7/ 129.8 (aromat. CH), 135.7/ 145.6 (aromat. C<sub>q</sub>), 191.3 (CHO). FD-MS: m/z (%) 220 (100, M<sup>+</sup>). IR (neat):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2930, 2860, 1685, 1600, 1205, 1120, 1030. Anal. Calc. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C 70.89; H 7.32. Found: C 70.98; H 7.12.

**(E,E,E)-1,3,5-Tris{2-[4-(3,4,5,6-tetrahydro-2H-pyran-2-yloxymethyl)phenyl]ethenyl}benzene (6)**: To the stirred suspension of 2.0 g (18 mmol) of KOC(CH<sub>3</sub>) in 80 ml of dry THF a solution of 2.3 g (4.4 mmol) of triphosphonate **5**<sup>2</sup> and 2.9 g (13.2 mmol) of **4** in 20 ml of THF was dropped at 0 °C under argon. The reaction

mixture was allowed to come to room temperature and the stirring continued for 12 h. The crude product was filtered over basic  $\text{Al}_2\text{O}_3$  (8 x 5 cm), eluted with diethyl ether and recrystallized from toluene to yield 2.75 g (87%) of a colorless solid (m.p. 165 °C).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.56 – 1.85 (m, 18 H,  $\text{CH}_2$ ), 3.55/ 3.92 (m, 6 H,  $\text{OCH}_2$ ), 4.51/ 4.79 (d, 6 H,  $\text{ArCH}_2\text{O}$ ), 4.72 (t, 3 H,  $\text{OCH}$ ), 7.11/ 7.21 (AB,  $^3J = 16.1$  Hz, 6 H, olefin. H), 7.37/ 7.53 (AA'BB', 12 H, aromat. H), 7.54 (s, 3 H, aromat. H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.3/ 25.4/ 30.5 ( $\text{CH}_2$ ), 62.1/ 68.6 ( $\text{OCH}_2$ ), 97.7 ( $\text{OCH}$ ), 123.9/ 126.5/ 128.2/ 128.2/ 128.9 (aromat. and olefin. CH), 136.5/ 137.8/ 137.9 (aromat.  $\text{C}_q$ ). FD-MS:  $m/z$  (%) 726 (100,  $\text{M}^+$ ). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3000, 2920, 2850, 1585, 1030, 955. Anal. Calc. for  $\text{C}_{48}\text{H}_{54}\text{O}_6$ : C 79.31; H 7.49. Found: C 79.27; H 7.88.

**Diethyl (*E,E,E*)-4-{2-[3,5-bis{2-[4-(diethoxyphosphorylmethyl)phenyl]ethenyl}phenyl]ethenyl}benzyl-**

**phosphonate (7):** To 2.48 g (3.41 mmol) of **6** dissolved in 60 ml of  $\text{CH}_2\text{Cl}_2$  50 ml (12.0 mmol) of triphenylphosphine dibromide in 50 ml of  $\text{CH}_2\text{Cl}_2$  was added.<sup>17</sup> The mixture was stirred at room temperature for 30 min. The solvent was evaporated, the residue dissolved in 3.7 g (22.0 mmol) of  $\text{P}(\text{OC}_2\text{H}_5)_3$  and heated to 160 °C for 3 h. Chromatography on silica gel (5 x 20 cm) gave with ethanol/ ethyl acetate (1 : 6) 2.01 g (73 %) of an oily product, which solidified after a few days, m. p. 140–144 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t, 18 H,  $\text{CH}_3$ ), 3.13 (d,  $^2J(\text{PH}) = 21.7$  Hz, 6 H,  $\text{CH}_2\text{P}$ ), 3.99 (m, 12 H,  $\text{OCH}_2$ ), 7.08/ 7.14 (AB,  $^3J = 16.4$  Hz, 6 H, olefin. H), 7.28/ 7.46 (AA'BB', 12 H, aromat. H), 7.49 (s, 3 H, aromat. H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  16.2 ( $\text{CH}_3$ ), 32.6 ( $\text{PCH}_2$ ), 62.1 ( $\text{OCH}_2$ ), 123.9/ 126.7/ 128.2/ 128.9/ 130.1 (aromat. and olefin. CH), 131.2/ 135.9/ 138.1 (aromat.  $\text{C}_q$ ). FD-MS:  $m/z$  (%) 834 (100,  $\text{M}^+$ ). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3010, 2975, 2900, 1580, 1500, 1240, 1050, 1025, 960, 850. Anal. Calc. for  $\text{C}_{45}\text{H}_{57}\text{O}_9\text{P}_3$ : C 64.74; H 6.88. Found: C 64.45; H 6.97.

**(*E*)-4-[2-(3,4,5-Tripropoxyphenyl)ethenyl]benzaldehyde (9a):** The procedure described for **6** was applied to 7.5 g (19 mmol) of diethyl 3,4,5-tripropoxybenzylphosphonate (**8a**), 4.1 g (20 mmol) of **3** and 5.0 g (45 mmol) of  $\text{KOC}(\text{CH}_3)_3$  in 80 ml of THF. The crude product was purified by column chromatography on silica gel (10 x 20 cm) with light petroleum/ ethyl acetate (5 : 1) to yield 4.81 g (66 %) of a pale yellow solid, m.p. 62 °C (DSC).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.06 (m, 9 H,  $\text{CH}_3$ ), 1.83 (m, 6 H,  $\text{CH}_2$ ), 3.97/ 3.99 (2 t, 6 H,  $\text{OCH}_2$ ), 6.73 (s, 2 H, aromat. H), 6.98/ 7.15 (AB,  $^3J = 16.4$  Hz, 2 H, olefin. H), 7.61/ 7.84 (AA'BB', 4 H, aromat. H), 9.97 (s, 1 H, CHO).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.6 ( $\text{CH}_3$ ), 22.7/ 23.5 ( $\text{CH}_2$ ), 70.8/ 75.1 ( $\text{OCH}_2$ ), 105.7/ 126.2/ 132.4/ 126.7/ 130.2 (aromat. and olefin. CH), 131.7/ 135.1/ 139.1/ 143.5/ 153.3 (aromat.  $\text{C}_q$ ), 191.5 (CHO). EI-MS:  $m/z$  (%) 382 (100,  $\text{M}^+$ ), 340 (48,  $[\text{M}-\text{C}_3\text{H}_6]^+$ ) 256 (27). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3020, 2960, 2920, 2860, 1690, 1590, 1575, 1555, 1120, 960, 830. Anal. Calc. for  $\text{C}_{24}\text{H}_{30}\text{O}_4$ : C 75.36; H 7.91. Found: C 75.32; H 7.92.

**(E)-4-[2-(3,4,5-Trihexyloxyphenyl)ethenyl]benzaldehyde (9b):** The compound was prepared according to the synthesis of **9a** and purified by column chromatography on silica gel (10 x 20 cm) with light petroleum/ acetone (15 : 1). Yield 79 %, yellow solid, m.p. 36 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.89 (m, 9 H, CH<sub>3</sub>), 1.32/ 1.47 (m, 18 H, CH<sub>2</sub>), 1.77 (m, 6 H, β-CH<sub>2</sub>), 3.97/ 4.01 (t, 6 H, OCH<sub>2</sub>), 6.72 (s, 2 H, arom. H), 6.98/ 7.15 (AB, <sup>3</sup>J = 16.4 Hz, 2 H, olefin. H), 7.61/ 7.84 (AA'BB', 4 H, arom. H), 9.96 (s, 1 H, CHO). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 22.6 - 31.7 (CH<sub>2</sub>), 69.2/ 73.6 (OCH<sub>2</sub>), 105.6/ 126.2/ 132.4/ 126.7/ 130.2 (aromat. and olefin. CH), 131.7/ 135.1/ 139.1/ 143.5/ 153.4 (aromat. C<sub>q</sub>), 191.5 (CHO). FD-MS: *m/z* (%) 508 (100, M<sup>+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2960, 2920, 2860, 1690, 1595, 1570, 1555, 1110, 960, 830. Anal. Calc. for C<sub>33</sub>H<sub>48</sub>O<sub>4</sub>: C 77.91; H 9.51. Found: C 77.98; H 9.52.

**(E)-4-[2-(3,4,5-Tridodecyloxyphenyl)ethenyl]benzaldehyde (9c):** The compound was prepared and purified according to **9b**. Yield 94 %, pale yellow solid, m.p. 43 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.86 (t, 9 H, CH<sub>3</sub>), 1.15 - 1.88 (m, 60 H, CH<sub>2</sub>), 4.01 (m, 6 H, OCH<sub>2</sub>), 6.72 (s, 2 H, arom. H), 6.98/ 7.15 (AB, <sup>3</sup>J = 16.4 Hz, 2 H, olefin. H), 7.61/ 7.84 (AA'BB', 4 H, arom. H), 9.96 (s, 1 H, CHO). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 14.1 (CH<sub>3</sub>), 22.6 - 31.7 (CH<sub>2</sub>), 69.2/ 73.6 (OCH<sub>2</sub>), 105.6/ 126.2/ 132.5/ 126.7/ 130.2 (aromat. and olefin. CH), 131.7/ 135.1/ 139.1/ 143.6/ 153.4 (aromat. C<sub>q</sub>), 191.5 (CHO). FD-MS: *m/z* (%) 761 (100, M<sup>+</sup>). IR (KBr)  $\tilde{\nu}$  [cm<sup>-1</sup>] 2920, 2840, 1690, 1590, 1570, 1555, 1120, 960, 830. Anal. Calc. for C<sub>51</sub>H<sub>84</sub>O<sub>4</sub>: C 80.47; H 11.12. Found: C 80.17; H 11.31.

**(E,E)-3,5-Bis{2-[4-[2-(3,4,5-tripropoxyphenyl)ethenyl]phenyl]ethenyl}benzaldehyde (11a):** The preparation was performed according to the procedure for **6**; 1.5 g (3.25 mmol) of **10**<sup>2</sup>, 2.5 g (6.53 mmol) of **9a**, 2.0 g (18.0 mmol) of KOC(CH<sub>3</sub>)<sub>3</sub> in 60 ml of THF yielded 2.0 g (71%) of **11a**. The product was recrystallized from chloroform, to which ethanol was added, till the solution became turbid. The compound has a clearing point of 136 °C (DSC). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 1.06 (m, 18 H, CH<sub>3</sub>), 1.83 (m, 12 H, CH<sub>2</sub>), 3.95/ 4.00 (2 t, 12 H, OCH<sub>2</sub>), 6.72 (s, 4 H, arom. H), 6.95/ 7.06 (AB, <sup>3</sup>J = 16.4 Hz, 4 H, olefin. H), 7.15/ 7.25 (AB, <sup>3</sup>J = 16.4 Hz, 4 H, olefin. H), 7.51 (AA'BB', 8 H, arom. H), 7.84, "s", 1 H/ 7.90 "s", 2 H (aromat. H), 10.07 (s, 1 H, CHO). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.5/ 10.6 (CH<sub>3</sub>), 22.8/ 23.5 (CH<sub>2</sub>), 70.9/ 75.1 (OCH<sub>2</sub>), 105.6/ 126.1/ 126.7/ 126.7/ 127.0/ 127.1/ 129.2/ 130.1/ 130.2 (aromat. and olefin. CH), 132.4/ 135.8/ 137.3/ 137.4/ 138.7/ 138.8/ 153.3 (aromat. C<sub>q</sub>), 192.1 (CHO). FD-MS: *m/z* (%) 864 (100, M<sup>+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3000, 2945, 2920, 2860, 1685, 1570, 1120, 950. Anal. Calc. for C<sub>57</sub>H<sub>66</sub>O<sub>7</sub>: C 79.32; H 7.71. Found: C 79.29; H 7.80.

**(E,E)-3,5-Bis{2-[4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]phenyl]ethenyl}benzaldehyde (11b):** Preparation and purification according to **11a**. Yield 83%, yellow solid, clearing point 113 °C (DSC). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.90 (m, 18 H, CH<sub>3</sub>), 1.33 (m, 24 H, CH<sub>2</sub>), 1.48 (m, 12 H, γ-CH<sub>2</sub>), 1.81/ 1.74 (m, 12 H, β-CH<sub>2</sub>),

3.96/ 4.01 (2 t, 12 H, OCH<sub>2</sub>), 6.71 (s, 4 H, arom. H), 6.96/ 7.04 (AB, <sup>3</sup>J = 16.2 Hz, 4 H, olefin. H), 7.15 (AB, <sup>3</sup>J = 16.2 Hz, 4 H), 7.51 (AA'BB', 8 H, arom. H), 7.83, "s", 1 H/ 7.89 "s", 2 H (aromat. H), 10.06 (s, 1 H, CHO). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.0/ 14.1 (CH<sub>3</sub>), 22.0-32.0 (CH<sub>2</sub>), 69.2/ 73.5 (OCH<sub>2</sub>), 105.3/ 126.2/ 126.7/ 126.8/ 127.1/ 127.1/ 129.2/ 130.1/ 130.2 (aromat. and olefin. CH), 132.4/ 135.8/ 137.2/ 137.4/ 138.5/ 138.7/ 153.3 (aromat. C<sub>q</sub>), 192.2 (CHO). FD-MS: *m/z* (%) 1116 (100, M<sup>+</sup>), 558 (36, M<sup>2+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3020, 2940, 2929, 2860, 1690, 1570, 1120, 950. Anal. Calc. for C<sub>75</sub>H<sub>102</sub>O<sub>7</sub>: C 80.75; H 9.22. Found: C 79.91; H 9.06.

**(*E,E*)-3,5-Bis{2-[4-[2-(3,4,5-tridodecyloxyphenyl)ethenyl]phenyl]ethenyl}benzaldehyde (11c):** Preparation and purification according to **11a**. Yield 57%, yellow solid, clearing point 104 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.86 (t, 18 H, CH<sub>3</sub>), 1.10 - 1.90 (m, 120 H, CH<sub>2</sub>), 4.01 (m, 12 H, OCH<sub>2</sub>), 6.71 (s, 4 H, arom. H), 6.99/ 7.01 (AB, <sup>3</sup>J = 16.1 Hz, 4 H, olefin. H), 7.19/ 7.21 (AB, <sup>3</sup>J = 16.1 Hz, 4 H, olefin. H), 7.51 (AA'BB', 8 H, arom. H), 7.85, "s", 1 H/ 7.89 "s", 2 H, (aromat. H), 10.07 (s, 1 H, CHO). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 22.0-32.0 (CH<sub>2</sub>), 69.3/ 73.5 (OCH<sub>2</sub>), 105.6/ 126.2/ 126.7/ 126.8/ 127.1/ 127.1/ 129.3/ 130.1/ 130.3 (aromat. and olefin. CH), 132.4/ 135.8/ 137.3/ 137.5/ 138.77/ 138.82/ 153.4 (aromat. C<sub>q</sub>), 192.0 (CHO). FD-MS: *m/z* (%) 1619 (55, M<sup>+</sup>), 810 (100, M<sup>2+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3010, 2910, 2840, 1690, 1570, 1115, 950. Anal. Calc. for C<sub>111</sub>H<sub>174</sub>O<sub>7</sub>: C 82.27; H 10.82. Found: C 82.18; H 10.84.

**(*E,E,E,E,E*)-1,3,5-Tris{2-[4-[2-(3,4,5-tripropoxyphenyl)ethenyl]phenyl]ethenyl}benzene**

**[9]-Cascade:benzene[3-1,3,5]:(5-[(*E*)-1-{4-[(*E*)-1-ethenyl]phenyl}ethenyl]-1,2,3-phenylene):4-oxabutane**

**(2a):** Dendrimer **2a** was prepared by applying the procedure for **6** to a solution of 218 mg (0.41 mmol) of **5** and 474 mg (1.24 mmol) of **9a** in 20 ml THF and a suspension of 2.0 g (18.0 mmol) of KOC(CH<sub>3</sub>)<sub>3</sub> in 60 ml of THF. The crude product was dissolved in CHCl<sub>3</sub> and precipitated by cautious addition of ethanol. Yield 440 mg (88 %), yellow solid, m.p. 216 °C (DSC). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 1.06 (m, 27 H, CH<sub>3</sub>), 1.83 (m, 18 H, CH<sub>2</sub>), 3.96/ 3.99 (2 t, 18 H, OCH<sub>2</sub>), 6.72 (s, 6 H, arom. H), 6.92/ 6.96 (AB, <sup>3</sup>J = 16.1 Hz, 6 H, olefin. H), 6.96/ 7.04 (AB, <sup>3</sup>J = 16.2 Hz, 6 H, olefin. H), 7.52 (AA'BB', 12 H, arom. H), 7.54 (s, 3 H, arom. H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 10.7 (CH<sub>3</sub>), 22.8/ 23.5 (CH<sub>2</sub>), 70.8/ 75.2 (OCH<sub>2</sub>), 105.4/ 124.0/ 126.8/ 127.0/ 127.3/ 128.2/ 129.0/ 129.0 (aromat. CH), 132.6/ 136.4/ 137.0/ 138.1/ 138.7/ 153.3 (aromat. C<sub>q</sub>). FD-MS: *m/z* (%) 1213 (100, M<sup>+</sup>), 606 (19, M<sup>2+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3010, 2950, 2920, 2860, 1570, 1115, 950. Anal. Calc. for C<sub>81</sub>H<sub>96</sub>O<sub>9</sub>: C 80.16; H 7.97. Found: C 79.75; H 8.10.

**(*E,E,E,E,E*)-1,3,5-Tris{2-[4-[2-(3,4,5-trihexyloxyphenyl)ethenyl]phenyl]ethenyl}benzene**

**[9]-Cascade:benzene[3-1,3,5]:(5-[(*E*)-1-{4-[(*E*)-1-ethenyl]phenyl}ethenyl]-1,2,3-phenylene):7-oxaheptane**

**(2b):** The dendrimer **2b** was prepared by using the procedure described for **2a**. Yield 61 %, yellow solid,

clearing point 129 °C (DSC).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.91 (m, 27 H,  $\text{CH}_3$ ), 1.35/ 1.49 (m, 54 H,  $\text{CH}_2$ ), 1.76/ 1.82 (m, 18 H,  $\beta\text{-CH}_2$ ), 3.97/ 4.02 (2 t, 18 H,  $\text{OCH}_2$ ), 6.71 (s, 6 H, arom. H), 6.96/ 7.03 (AB,  $^3J = 16.1$  Hz, 6 H, olefin. H), 7.13/ 7.18 (AB,  $^3J = 16.0$  Hz, 6 H, olefin. H), 7.49/ 7.53 (AA'BB', 12 H, arom. H), 7.53 (s, 3 H, arom. H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0 ( $\text{CH}_3$ ), 22.0 - 32.0 ( $\text{CH}_2$ ), 69.3/ 73.6 ( $\text{OCH}_2$ ), 105.5/ 124.0/ 126.8/ 127.0/ 127.3/ 128.2/ 128.9/ 129.0 (aromat. and olefin. CH), 132.6/ 136.4/ 137.1/ 138.2/ 138.7/ 153.4 (aromat.  $\text{C}_q$ ). FD-MS:  $m/z$  (%) 1592 (75,  $\text{M}^+$ ), 796 (100,  $\text{M}^{2+}$ ). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3010, 2950, 2920, 2850, 1570, 1110, 955. Anal. Calc. for  $\text{C}_{108}\text{H}_{150}\text{O}_9$ : C 81.46; H 9.49. Found: C 81.50; H 9.40.

**(*E,E,E,E,E*)-1,3,5-Tris{2-[4-[2-(3,4,5-tridodecyloxyphenyl)ethenyl]phenyl]ethenyl}benzene**

**[9]-Cascade:benzene[3-1,3,5]:(5-[(*E*)-1-[4-((*E*)-1-ethenyl)phenyl]ethenyl]-1,2,3-phenylene):13-**

**oxatridecane (2c):** The dendrimer **2c** was prepared by applying the procedure described for **2a,b**; however, NaH was used instead of  $\text{KOC}(\text{CH}_3)_3$ . Yield 60 %, yellow solid, clearing point 108 °C (DSC).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.88 (t, 27 H,  $\text{CH}_3$ ), 1.17 - 1.86 (m, 180 H,  $\text{CH}_2$ ), 3.97/ 4.02 (2 t, 18 H,  $\text{OCH}_2$ ), 6.71 (s, 6 H, arom. H), 6.97/ 7.03 (AB,  $^3J = 16.1$  Hz, 6 H, olefin. H), 7.14/ 7.20 (AB,  $^3J = 16.4$  Hz, 6 H, olefin. H), 7.50/ 7.53 (AA'BB', 12 H, arom. H), 7.55 (s, 3 H, arom. H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1 ( $\text{CH}_3$ ), 22.0 - 32.0 ( $\text{CH}_2$ ), 69.3/ 73.6 ( $\text{OCH}_2$ ), 105.5/ 123.9/ 126.7/ 126.9/ 127.2/ 128.2/129.0/ 129.0 (aromat. and olefin. CH), 132.5/ 136.4/ 137.0/ 138.2/ 138.7/ 153.4 (aromat.  $\text{C}_q$ ). FD-MS:  $m/z$  (%) 2349 (17,  $\text{M}^+$ ), 1174 (100,  $\text{M}^{2+}$ ). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3020, 2930, 2850, 1570, 1115, 960. Anal. Calc. for  $\text{C}_{162}\text{H}_{258}\text{O}_9$ : C 82.81; H 11.07. Found: C 82.75; H 10.96

**(*all-E*)-1,3,5-Tris{2-[4-[2-[3,5-bis{2-[4-[2-(3,4,5-tripropoxyphenyl)ethenyl]phenyl]ethenyl]phenyl]ethenyl]phenyl]ethenyl}benzene**

**[18]-Cascade:benzene[3-1,3,5]:(5-[(*E*)-1-[4-((*E*)-1-ethenyl)phenyl]ethenyl]-1,3-phenylene):(5-[(*E*)-1-[4-((*E*)-1-ethenyl)phenyl]ethenyl]-1,2,3-phenylene):4-oxabutane (2a')**

**(2a')** The procedure for the preparation of **6** was applied to a solution of 156 mg (0.19 mmol) of **7** and 500 mg (0.58 mmol) of **11a** in 10 ml of THF and a suspension of 2.0 g (18.0 mmol) of  $\text{KOC}(\text{CH}_3)_3$  in 40 ml of THF. The crude yellow powder was recrystallized from THF. Yield 313 mg (57%), clearing point 254 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.03 (t, 54 H,  $\text{CH}_3$ ), 1.78/ 1.80 (m, 36 H,  $\text{CH}_2$ ), 3.94 (t, 36 H,  $\text{OCH}_2$ ), 6.67 (s, 12 H, arom. H), 6.91/ 6.97 (AB,  $^3J = 16.2$  Hz, 12 H, olefin. H), 6.98/ 7.03 (AB,  $^3J = 16.2$  Hz, 24 H, olefin. H), 7.32 - 7.50 (m, 48 H, arom. H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.6 ( $\text{CH}_3$ ), 22.9/ 23.6 ( $\text{CH}_2$ ), 70.9/ 75.2 ( $\text{OCH}_2$ ), 105.7/ 124.0/ 124.0/ 124.0/ 126.8/ 126.8/ 127.0/ 127.0/ 127.3/ 128.2/ 128.3/ 128.6/ 128.7/ 128.8/ 129.0/ 129.0 (aromat. and olefin. CH), 132.5/ 136.4/ 136.6/ 136.7/ 137.0/ 137.9/ 138.0/ 138.1/ 138.8/ 153.4 (aromat.  $\text{C}_q$ ). FD-MS:  $m/z$  (%) 2962 (2,  $\text{M}^+$ ), 1480 (29,  $\text{M}^{2+}$ ), 987 (100,  $\text{M}^{3+}$ ). IR (KBr):  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3010, 2960, 2920, 2860, 1570, 1115, 955. Anal. Calc. for  $\text{C}_{204}\text{H}_{222}\text{O}_{18}$ : C 82.72; H 7.55. Found: C 82.15; H 7.56.



**(all-E)-1,3,5-Tris{2-[4-{2-[3,5-bis{2-[4-(2-(3,4,5-trihexyloxyphenyl)ethenyl)phenyl]ethenyl}phenyl]ethenyl}phenyl]ethenyl}benzene**

**[18]-Cascade:benzene[3-1,3,5]:(5-[(E)-1-{4-((E)-1-ethenyl)phenyl}ethenyl]-1,3-phenylene):(5-[(E)-1-{4-((E)-1-ethenyl)phenyl}ethenyl]-1,2,3-phenylene):7-oxaheptane (2b')**: The compound was prepared according to the synthesis of 2a'. The product was recrystallized from ethyl acetate/ methanol (2 : 1). Yield 48%, yellow powder, clearing point 235 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.91 (m, 54 H, CH<sub>3</sub>), 1.34/ 1.47 (m, 108 H, CH<sub>2</sub>), 1.78 (m, 36 H, β-CH<sub>2</sub>), 3.95 (m, 36 H, OCH<sub>2</sub>), 6.66 (s, 12 H, aromat. H), 6.80 - 7.10 (m, 36 H, olefin. H), 7.20 - 7.50 (m, 48 H, aromat. H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.0/ 14.1 (CH<sub>3</sub>), 22.6 - 31.8 (CH<sub>2</sub>), 69.2/ 73.5 (OCH<sub>2</sub>), 105.4/ 124.0/ 124.0/ 126.7/ 126.7/ 127.0/ 127.0/ 127.1/ 128.1/ 128.2/ 128.8/ 128.9/ 128.9 (aromat. and olefin. CH, partly superimposed), 132.5/ 136.3/ 136.5/ 136.8/ 137.7/ 137.8/ 137.9/ 138.5/ 153.3 (aromat. C<sub>q</sub>, partly superimposed). MS (MALDI-TOF, dithranol): *m/z* (%) 3719 (M<sup>+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3010, 2950, 2920, 2860, 1575, 1110, 955. Anal. Calc. for C<sub>258</sub>H<sub>330</sub>O<sub>18</sub>: C 83.31; H 8.94. Found: C 83.48; H 8.94.

**(all-E)-1,3,5-Tris{2-[4-{2-[3,5-bis{2-[4-(2-(3,4,5-tridodecyloxyphenyl)ethenyl)phenyl]ethenyl}phenyl]ethenyl}phenyl]ethenyl}benzene**

**[18]-Cascade:benzene[3-1,3,5]:(5-[(E)-1-{4-((E)-1-ethenyl)phenyl}ethenyl]-1,3-phenylene):(5-[(E)-1-{4-((E)-1-ethenyl)phenyl}ethenyl]-1,2,3-phenylene):13-oxatridecane (2c')**: The compound was prepared according to the synthesis of 2a'. A yellow, waxy solid was isolated; yield 55%, clearing point 195 °C. <sup>1</sup>H NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 140 °C): δ 0.93 (t, 54 H, CH<sub>3</sub>), 1.30-1.60 (m, 324 H, CH<sub>2</sub>), 1.80/ 1.85 (m, 36 H, β-CH<sub>2</sub>), 4.04/ 4.08 (2 t, 36 H, OCH<sub>2</sub>), 6.76 (s, 12 H, aromat. H), 6.98/ 7.04 (AB, <sup>3</sup>J = 16.2 Hz, 12 H, olefin. H), 7.19/ 7.23 (AB, <sup>3</sup>J = 16.2 Hz, 12 H, olefin. H), 7.23/ 7.25 (AB, <sup>3</sup>J = 16.0 Hz, 6 H, olefin. H), 7.24/ 7.26 (AB, <sup>3</sup>J = 15.9 Hz, 6 H, olefin. H), 7.52/ 7.56 (AA'BB', 24 H, aromat. H), 7.58-7.63 (m, 24 H, aromat. H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.1 (CH<sub>3</sub>), 22.0 - 32.0 (CH<sub>2</sub>), 69.3/ 73.6 (OCH<sub>2</sub>), 105.5/ 124.0/ 126.8/ 127.0/ 127.2/ 128.1/ 128.3/ 128.8/ 128.7/ 128.8/ 129.0 (aromat. and olefin. CH, partly superimposed), 132.5/ 136.4/ 136.7/ 137.0/ 138.0/ 138.1/ 138.7/ 153.4 (aromat. C<sub>q</sub>, partly superimposed). MS (MALDI-TOF, dithranol): *m/z* (%) 5235 (M<sup>+</sup>). IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3020, 2920, 2850, 1575, 1115, 960. Anal. Calc. for C<sub>366</sub>H<sub>546</sub>O<sub>18</sub>: C 83.98; H 10.51. Found: C 83.87; H 10.57.

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**References and Notes**

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